INTERNATIONAL ATOMIC WEIGHTS

Based on C^{12}

Element	*Symbol*	*Atomic number*	*Atomic weight*	*Element*	*Symbol*	*Atomic number*	*Atomic weight*
Actinium	Ac	89	[227]*	Mercury	Hg	80	200 59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	[243]*	Neodymium	Nd	60	144 24
Antimony	Sb	51	121.75	Neon	Ne	10	20 183
Argon	Ar	18	39.948	Neptunium	Np	93	[237]*
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	[210]*	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	[247]*	Nobelium	No	102	[254]*
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15 9994
Boron	B	5	10 811	Palladium	Pd	46	106.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112 40	Platinum	Pt	78	195.09
Calcium	Ca	20	40 08	Plutonium	Pu	94	[242]*
Californium	Cf	98	[247]*	Polonium	Po	84	[210]
Carbon	C	6	12.01115	Potassium	K	19	39.102
Cerium	Ce	58	140 12	Praseodymium	Pr	59	140.907
Cesium	Cs	55	132 905	Promethium	Pm	61	[147]*
Chlorine	Cl	17	35 453	Protoactinium	Pa	91	[231]*
Chromium	Cr	24	51.996	Radium	Ra	88	[226]*
Cobalt	Co	27	58.9332	Radon	Rn	86	[222]*
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96	[247]*	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	[254]*	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44 956
Fermium	Fm	100	[253]*	Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	[223]*	Silver	Ag	47	107.870
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	[97]*
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lw	103	[257]*	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	[256]*				

*Mass numbers of the most stable or most abundant isotopes are shown in parentheses.

CHEMICAL PRINCIPLES

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A Programmed Text

by

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Burgess Publishing Company

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PREFACE

An understanding and appreciation of science and the scientific method requires much more than the mere memorization and cataloguing of factual data Ability to grasp concepts and dexterity in proposing solutions to problems are some of the essential characteristics which need to be developed. The primary purpose of this book is to assist the student in developing those characteristics so essential for solving new problems and interpreting unfamiliar data.

This is a programmed book It is organized into a logical set of questions which, when answered correctly, will lead the students to the desired learning goal Each question is accompanied by a correct response so that proposed answers may be immediately checked. This book differs from many programmed texts in that topics are covered in more depth and the questions require a greater degree of independent thought. Some questions may be answered quickly Other questions are more involved and will require plotting of graphs, solving quadratic equations, or deriving mathematical relationships.

This programmed book is divided into 10 chapters, each of which has a short introduction indicating what should be accomplished. Following the introduction are statements (marked S), questions (marked Q), answers (marked A) and review statements (marked R) The statements give some basic information and are followed by a series of graded questions and answers. <u>This manual will be a useful learning aid only if each question is answered by the student before the correct response is consulted</u> Reading the question and then reading the answer <u>is not</u> satisfactory. The following steps are recommended for using this book·

1. Cover each page of the book with a piece of scratch paper in such a way that you can see only a statement. Read the statement carefully.

2. Uncover the first question. <u>Write out</u> the answer to the question on the piece of scratch paper.

3. Move the scratch paper down the page so that a correct response to the first question can be seen. Read the entire answer given and compare it with your answer.

4. If your answer is correct, proceed to the next question. If your answer is incorrect, restudy the previous statement and questions. DO NOT PROCEED UNTIL YOU UNDERSTAND AND CAN CORRECTLY ANSWER EACH QUESTION.

This programmed book will assist you in learning the principles of chemistry; however, it is not a substitute for hard and diligent work.

We are indebted to the helpful suggestions made by colleagues and the many students at Hamline University who have used this book. We wish to particularly thank Dr. Perry Moore, Dr Rodney Olsen, Dr. Lyle Hall, Miss Elain Folkers, Miss Kathlyn Deviny and Mr. Roger Giese for their assistance. We gratefully acknowledge the financial support of the Louis W. and Maud Hill Family Foundation in the preparation of the manuscript.

O. R.
C. J. C.
J. T. H.

TABLE OF CONTENTS

Chapter 1 | *MATHEMATICAL MANIPULATIONS*

This chapter is divided into four parts. Even though certain topics may have been studied previously and seem familiar, you should be sure that each problem in every part can be worked quickly and accurately.

Part I: Scientific Notation and Logarithms

After completing this section you should be able to

a) express any number in scientific notation
b) determine the logarithm and anti-logarithm of any number
c) use logs to multiply or divide any two numbers
d) use logs to determine the value of a number raised to any power.

Part II: The Slide Rule

After completing this section you should be able to

a) use the slide rule to multiply or divide any two numbers
b) use the slide rule to find the log and anti-log of any number
c) use the slide rule to find squares, cubes, square roots and cube roots of any number.

Part III: Treatment of Experimental Data

After completing this section you should be able to

a) determine the number of significant figures in any number
b) determine the significant figures in an answer after an addition, subtraction, multiplication or division process
c) compute deviations
d) understand the significance of a deviation.

Part IV: Units and the Unit Conversion Method

After completing this section you should be able to solve problems by the unit conversion method.

PART I: Scientific Notation and Logarithms

S-1 The study of science deals with very large and very small numbers. It is important, therefore, that we learn how to manipulate these large and small numbers without error. Numbers can be expressed as a unit number (a number between one and ten which may be a decimal, e.g., 7.62) times some power of ten (i.e., in <u>scientific notation</u>). The exponent of ten is determined by the number of places the decimal point must be moved in order to form the unit number. For every place the decimal is moved to the left, the exponent is increased by one unit. For every place the decimal is moved to the right, the exponent is reduced by one unit. For example

$$0.00378 = 3.78 \times 10^{-3}$$
$$651 = 6.51 \times 10^{2}$$
$$0.087 \times 10^{8} = 8.7 \times 10^{6}$$

	Q-1 Write the following numbers in scientific notation. a) 0.0000695 b) 0.0000000732
A-1 a) 6.95×10^{-5} b) 7.32×10^{-8}	Q-2 Write the following numbers in scientific notation. a) 624200.0 b) 380090600.0
A-2 a) 6.242×10^{5} b) 3.800906×10^{8}	Q-3 Write the following numbers in scientific notation. a) 0.0275×10^{3} b) 0.00769×10^{-2}
A-3 a) 2.75×10^{1} b) 7.69×10^{-5}	Q-4 Write the following numbers in scientific notation. a) 38.76×10^{5} b) 7826.2×10^{-9}
A-4 a) 3.876×10^{6} b) 7.8262×10^{-6}	Q-5 Write the numerical equivalent of the following numbers in <u>non</u>-scientific notation. a) 7.32×10^{-2} b) 8.92×10^{4}
A-5 a) 0.0732 b) 89,200	Q-6 Write the numerical equivalent of the following numbers in <u>non</u>-scientific notation. a) 2.37×10^{10} b) 4.56×10^{-7}
A-6 a) 23,700,000,000 b) 0.000000456	

S-2 The logarithm of 10^9 is 9 000, the logarithm of 10^{23} is 23.000, and the logarithm of 10^{-6} is -6 000 The logarithm of a number is simply the power of ten that must be used to express that number The number 1, expressed as a power of ten, is 10^0, and the number ten, expressed as a power of ten, is 10^1 Any number between one and ten can be expressed as a power of ten and that power will be between zero and one. Thus, the number five, expressed as a power of ten, is $10^{0\ 699}$ Therefore, the log of five is 0.699 The log of a number is not readily computed, but fortunately the logs of numbers are provided in table form (A table of logarithms is provided at the end of this chapter.) The following example explains how to use this table. 3 74 expressed as a power of ten would be ten raised to the log of 3 74, i e., $10^{\log 3.74}$. To find the log of 3.74 in the table, follow these steps

a) find the first two digits of the number, i.e , 37, in the left hand column under N,
b) go directly across from this number until you are in the column headed by the third digit of the number, i.e., 4, the number in the column is the log of 3 74 (log 3 74 = 0.5729);
c) if the number had had four digits, say 3 742, proceed to the proportional parts table located on the right hand side of each page;
d) the number directly across from the log previously found and in the column headed by the fourth digit of the number (2) is, in this case, 0.0002 (the decimal and three zeros are understood) This proportional part is added to the log of 3.74,

$$\begin{array}{rl} 0.5729 & \text{(log 3.74)} \\ +0.0002 & \underline{\text{(proportional part)}} \\ \hline 0.5731 & \text{(log 3 742)} \end{array}$$

Q-7 Using the log table, find the log of each of the following·

a) 4.36
b) 7 77
c) 9.21

A-7 a) 0.6395
b) 0.8904
c) 0.9643

Q-8 Find the log of each of the following.

a) 2.762
b) 4.983
c) 9.762

A-8 a) 0.4409 + 0.0003 = 0.4412
b) 0.6972 + 0.0003 = 0.6975
c) 0.9894 + 0 0001 = 0.9895

Q-9 Express each of the following numbers as a power of ten.

a) 1.388
b) 2.179

A-9 To express a number as a power of ten is to raise ten to the log of the number.

a) log 1.388 = 0.1399 + 0.0026
= 0.1425
as a power of ten: $10^{0.1425}$
b) log 2.179 = 0.3365 + 0.0018
= 0 3383
as a power of ten: $10^{0.3383}$

Q-10 Find the log of each of the following.

a) 3.769
b) 5.890
c) 6.311

A-10 a) 0.5752 log 3.76
0.0010 proportional part
0.5762 log 3.769
b) 0.7701 log 5.890
c) 0.8000 log 6.31
0.0001 proportional part
0.8001 log 6.311

S-3 To find the log of a number less than one or larger than ten, write the number in scientific notation, i.e., as a unit numeral and a power of ten. The log of the numeral and the exponent of ten are <u>added</u>. For example

$$\begin{aligned} \log(3.61 \times 10^{3}) &= \log 3.61 + \log 10^{3} \\ &= 0.5575 + 3.000 \\ &= 3.5575 \end{aligned}$$

$$\begin{aligned} &\log 0.0361 \\ &= \log(3.61 \times 10^{-2}) \\ &= \log 3.61 + \log 10^{-2} \\ &= 0.5575 + (-2.000) \\ &= -1.4425 \end{aligned}$$

(Numbers to the left of the decimal are referred to as the characteristic of the log. The numbers to the right of the decimal are referred to as the mantissa.)

	Q-11 Find the log of 10,480
A-11 $\log(1.048 \times 10^{4}) = 4.000 + 0.0203 = 4.0203$	Q-12 Find the log of 0.000978.
A-12 $\log(9.78 \times 10^{-4}) = -4.000 + 0.9903 = -3.0097$	Q-13 Find the logs of each of the following numbers. a) 0.0917 b) 0.00627
A-13 a) $0.9624 + (-2.000) = -1.0376$ b) $0.7973 + (-3.000) = -2.2027$	Q-14 Find the logs of the following numbers. a) 38.16 b) 1002.0
A-14 a) $0.5816 + 1 = 1.5816$ b) $0.0008 + 3 = 3.0008$	Q-15 Give the logarithms of the following numbers. a) 0.0038 b) 1.37×10^{-6} c) 9.81×10^{-17}
A-15 a) $-3 + 0.5798 = -2.4202$ b) $-6 + 0.1367 = -5.8633$ c) $-17 + 0.9917 = -16.0083$	

S-4 If the logarithm of a number is given, the original number can be determined. That is, the <u>antilog</u> of the log can be determined. For example, to find the number whose log is 0.2480, first find the log in the body of the table and then determine the unit and tenth place of the number from the column headed N. The hundredth place of the number will be found at the heading of the column in which the logarithm is located. In the case of 0.2480, the antilog is 1.77. If the log had been 0.2487, the number would not have been found in the body of the table. The closest number listed which is <u>less</u> than 0.2487 is 0.2480, which differs from the correct log by 0.0007 units. Moving across the same row to the proportional parts table, find the number closest to 0.0007 and note that it is listed in the column headed 3. Therefore, the antilog of 0.2487 is 1.77<u>3</u>.

	Q-16 Find the antilog of the following numbers. a) 0 9106 b) 0.7860
A-16 a) 8 140 b) 6 110	Q-17 Find the antilog of the following numbers a) 0.0934 b) 0 8713
A-17 a) 1.240 b) 7.435	Q-18 Find the antilog of the following numbers a) 0.5748 b) 0.3287 c) 0.7358
A-18 a) 3.757 b) 2.132 c) 5.442	

S-5 To find the antilog of a log which is greater than one, e g. 2.8615, treat the log as the sum of an integer and a decimal (i e , 2 + 0.8615). Raise ten to the integer and find the antilog of the decimal portion. Finally, multiply these two together. For example·

2.8615 = 2 + 0.8615
antilog of 0.8615 = 7.270
therefore, antilog of 2.8615 = $10^2 \times 7.270$

	Q-19 Find the antilog of 1.1235.
A-19 1.1235 = 0.1235 + 1 antilog of 0.1235 = 1.329 antilog of 1.1235 = 1.329×10^1	Q-20 Find the antilog of 9.8764.
A-20 7.523×10^9	Q-21 Find the antilog of 13.4861.
A-21 3.063×10^{13}	Q-22 Find the antilog of 7.3712.
A-22 7.3712 = 0.3712 + 7 antilog of 0.3712 = 2.350 antilog of 7.3712 = 2.350×10^7	Q-23 Find the antilog of 23.7796.
A-23 23.7796 = 0.7796 + 23 antilog of 0.7796 = 6.020 antilog of 23.7796 = 6.020×10^{23}	

S-6 The logarithms listed in the table are positive values; therefore, negative logs cannot be found directly.
The antilog of a negative log such as -2.3201 is found in the following way. First rewrite the log as the sum of a negative whole number and a positive decimal (e.g., -3 +0.6799). Find the antilog of the decimal part (in this case 4.785) and then multiply this antilog times ten raised to the negative whole number. The antilog of -2.3201 then is 4.785×10^{-3}.

Q-24 What is the antilog of -7.320?

A-24 The logarithm -7.320 can be rewritten as -8 + 0.680. The antilog of -8 is 10^{-8}, the antilog of 0.680 is 4.79. Therefore, the antilog of -7.320 is 4.79×10^{-8}

Q-25 What is the antilog of -14.77?

A-25 -14.77 = -15 + 0.23
antilog of 0.23 = 1.70
antilog of -14.77 = 1.70×10^{-15}

Q-26 What is the antilog of each of the following?

a) -12.31
b) -2.78
c) -4.50

A-26 a) antilog of (-13 + 0.69) = 4.90×10^{-13}
b) antilog of (-3 + 0.22) = 1.66×10^{-3}
c) antilog of (-5 + 0.50) = 3.16×10^{-5}

Q-27 What is the antilog of each of the following?

a) -42.2534
b) -19.6073

A-27 a) antilog (-43 + 0.7466)
antilog 0.7466 = 5.580
antilog -42.2534 = 5.580×10^{-43}
b) antilog (-20 + 0.3927)
antilog 0.3927 = 2.470
antilog -19.6073 = 2.470×10^{-20}

S-7 Multiplication of powers of ten involves <u>adding</u> exponents. For example

$$10^2 \times 10^3 = 10^5$$
$$10^{17} \times 10^{10} = 10^{27}$$
$$10^{0.523} \times 10^{0.418} = 10^{0.941}$$

Because the exponents are the logarithms, numbers can be multiplied by adding their logarithms. For example, the value of (3.210)(2.520) may be found in the following way:

log 3.210 = 0.5065
log 2.520 = 0.4014
sum of logs = 0.9079
antilog of 0.9079 = 8.090
(3.210)(2.520) = 8.090

Q-28 Using logarithms carry out the following operation.

(1.23)(4.56)

A-28 0.0899 = log 1.23
0.6590 = log 4.56
0.7489
antilog 0.7489 = 5.609

Q-29 Using logs, multiply.

4.980 x 1.060

A-29 0.6972 = log 4.98
0.0253 = log 1.06
0.7225
antilog 0.7225 = 5.279

Q-30 Using logs, multiply.

3.860 x 2.150

A-30 $\;0\;5866 = \log 3\;86$
$\underline{0\;3324} = \log 2\;15$
$0\;9190$
antilog $0\;9190 = 8\;298$

Q-31 Using logs, multiply
$7\;985 \times 12\;36$

A-31 $0\;9022 = \log 7\;985$
$\underline{1.0920} = \log 12.36$
1.9942
antilog $1.9942 = 9.870 \times 10^1$

Q-32 Multiply using logs
$0\;00879 \times 0\;09634$

A-32 $0.9440 + (-3) = \log 0.00879$
$\underline{0.9838 + (-2)} = \log 0\;09634$
$1.9278 + (-5)$ or
$0\;9278 - 4$
antilog of $0\;9278 + (-4) = 8.468 \times 10^{-4}$

Q-33 Multiply using logs
$10\;95 \times 453\;2$

A-33 $1.0395 = \log 10\;95$
$\underline{2.6563} = \log 453.2$
3.6958
antilog of $3\;6958 = 4\;963 \times 10^3$

Q-34 Multiply using logs.
$987.2 \times 7,425$

A-34 $2.9944 = \log 987\;2$
$\underline{3.8707} = \log 7,425$
6.8651
antilog $6.8651 = 7.330 \times 10^6$

Q-35 Multiply using logs.
$0.00937 \times 0.000000581$

A-35 $0\;9717 + (-3) = \log 0.00937$
$\underline{0.7642 + (-7)} = \log 0.000000581$
$1.7359 + (-10)$
$0.7359 + (-9)$
antilog $= 5.444 \times 10^{-9}$

R. To multiply, add exponents or add logarithms.
$2.76 \times 7.84 = \text{antilog}\,[\log 2.87 + \log 7.84]$

S-8 To divide powers of ten, the exponents are subtracted. For example:

$$10^7 / 10^2 = 10^{7-2} = 10^5$$

$$10^{0.5321} / 10^{0.2876} = 10^{0.2445}$$

Because the exponents are logarithms, division can be carried out by subtracting logarithms. For example, the following operation is carried out in the manner indicated.

$$\frac{12.37}{1.430}: \quad \begin{aligned} \log 12.37 &= 1.0923 \\ -\log 1.430 &= \underline{-0.1553} \\ &\;\; 0.9370 \end{aligned}$$

antilog $0.9370 = 8.650$

Q-36 Using logs, divide $\frac{9372}{1865}$.

A-36 $\log 9372 = 3.9718$
$\log 1865 = \underline{-3.2707}$
0.7011
antilog of $0.7011 = 5.025$

Q-37 Using logs, divide $\frac{5286}{28.60}$.

A-37
log 5286 = 3.7231
log 28 60 = -1 4564
2 2667
antilog 2 2667 = 1.848 x 10^{2}

Q-38 Using logs, divide $\frac{8752}{0\ 00071}$

A-38
log 8752 = 0 9421 + 3
log 0 00071 = -0 8513 - (-4)
0 0908 + 7
antilog 7 0908 = 1 233 x 10^{7}

Q-39 Divide using logs

$$\frac{1\ 764 \times 10^{-10}}{3\ 89 \times 10^{-6}}$$

A-39
log 1 764 x 10^{-10} = 0 2465 + (-10)
log 3 89 x 10^{-6} = -0 5899 - (-6)
-0 3434 -4
antilog (-0 3434 -4) =
antilog (0 6566 -5)
= 4.535 x 10^{-5}

Q-40 Using logs, divide

$$\frac{0\ 00984}{0\ 000760}$$

A-40
log 0 00984 = 0 9930 + (-3)
log 0 000760 = -0 8808 - (-4)
0 1122 + 1
antilog 1 1122 = 1 295 x 10^{1}

Q-41 Using logs, divide

$$\frac{7\ 68 \times 10^{-5}}{1.92 \times 10^{14}}$$

A-41
log 7 68 x 10^{-5} = 0 8854 - 5
log 1 92 x 10^{14} = -(0 2833 + 14)
0 6021 - 19
antilog (0 6021 - 19) = 4 00 x 10^{-19}

R **To divide numbers, exponents are subtracted or logarithms are subtracted.**

3.92 ÷ 3.44 = antilog [log 3.92 - log 3.44]

S-9 Any root of a number, i e , square, cube, etc , can easily be found by using logs. First, find the log of the number. Then simply divide the log by the degree of the root. Finally, find the antilog For example

$\sqrt[7]{3879}$
a) log 3879 = 0 5887 + 3
b) $\frac{3\ 5887}{7}$ = 0.5127
c) antilog of 0 5127 = 3.256 = $\sqrt[7]{3879}$

If the original number is less than one, the log must be manipulated to be put in a usable form. For example

$\sqrt[5]{0\ 00692}$
a) log 0.00692 = 0 8401 - 3 = -2.1599 (The log must be expressed as one complete number, not as the sum of two numbers)
b) divide, as before, by the degree of the root $\frac{-2\ 1599}{5}$ = -0.4320
c) to find the antilog, first convert the log into the sum of a positive decimal and a whole number -0.4320 = 0.5680 - 1 and then determine the antilog which is 3.698 x 10^{-1}.

Q-42 Find the cube root of 389200, that is:

$$\sqrt[3]{389200}$$

A-42
a) log 389200 = 5.5901
b) $\frac{5\ 5901}{3}$ = 1.8634
c) antilog 1.8634 = 73.01

Q-43 Find $\sqrt[6]{1.976}$

A-43 a) log 1 976 = 0 2958
b) $\frac{0\ 2958}{6} = 0\ 0493$
c) antilog 0 0493 = 1 120

Q-44 Find $(0.000781)^{\frac{1}{2}}$, that is $\sqrt[2]{0\ 000781}$

A-44 a) log 0 000781 = 0 8927 + (-4)
b) $\frac{-3\ 1073}{2} = -1\ 5537$
c) antilog (-1 5537) = antilog (0.4463 - 2)
= $2\ 794 \times 10^{-2}$
= 0 02794

Q-45 Find $(0.00647)^{\frac{1}{9}}$, that is, $\sqrt[9]{0\ 00647}$

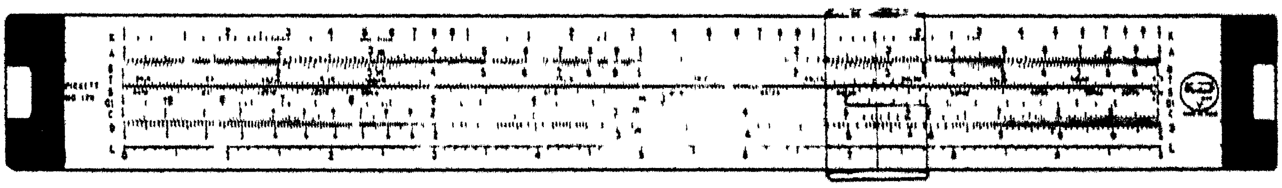
A-45 a) log 0 00647 = 0 8109 -3
= -2.1891
b) $\frac{-2\ 1891}{9} = -0\ 2432$
c) antilog -0 2432 = antilog (0.7568 - 1)
= 0.5713

R To find the root of a number, divide the log of the number by the root, then determine the antilog of the result.

$\sqrt[6]{3.217}$ = antilog [log 3.217 ÷ 6]

PART II: The Slide Rule

S-1 While numbers may be multiplied and divided by using logs, the slide rule is a still more convenient way to carry out these operations. For this part of the program you will need a slide rule which has C, D, L, A and K scales The relative positions of these scales on the slide rule are:



Q-1 Find the C, D, L, A, and K scales on your slide rule.

A-1 See S-1 for correct positions

S-2 The number 1 on the extreme left or right of the K, A, C, and D scales are called the <u>index lines</u>.

Q-2 Find the index lines on your slide rule.

A-2 See S-1.

Q-3 Find the movable hairline. Set the right index line of the C scale on the number 4 of the D scale.

S-3 The L scale is a <u>linear</u> scale, i.e., it is divided into ten equal linear parts, which are further subdivided. The L scale gives a direct reading of the logarithm of the number directly above it on the D scale. For example, if you set the hairline at two on the D scale, the reading on the L scale is 0.303 which is the logarithm of 2.0.

Q-4 Find the logarithm of 5 and of 7.

A-4 log 5 = 0.70
log 7 = 0.85

S-4 To find the antilog of a number, simply reverse the process of finding the logarithm. Thus, to find the antilog of 0.538, set the hairline at 0.538 on the L scale and read the antilog on the D scale.

Q-5 Find the antilog of
a) 0.232 b) 0.381

A-5 a) 1.71 b) 2.41

Q-6 Find the antilog of:
a) 0.562 b) 0.821

A-6 a) 3.65 b) 6.62

S-5 To find the logarithm of a number less than one or greater than ten, express the number in scientific notation. The log of the unit number is read off the slide rule as before.

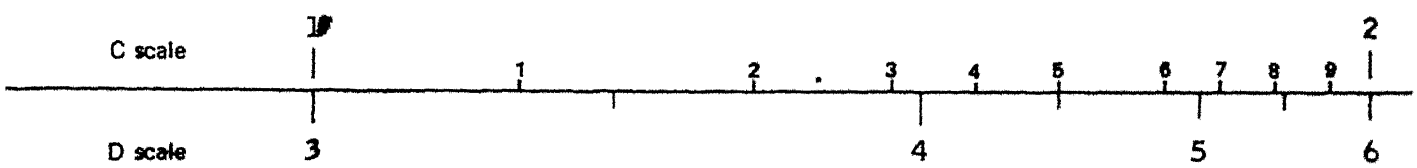
Q-7 Using your slide rule, find the log of:
a) 373.0 b) 0.000067

A-7 a) $\log 373.0 = \log 3.73 \times 10^2$
$= 0.572 + 2$
$= 2.572$
b) $\log 0.000067 = \log 6.7 \times 10^{-5}$
$= 0.826 - 5$
$= -4.174$

Q-8 Using your slide rule, find the antilog of:
a) 2.820 b) -3.914

A-8 a) antilog 2.820 = antilog (2 + 0.820)
$= 6.61 \times 10^2$
b) antilog -3.914 = antilog (-4 + 0.086)
$= 1.219 \times 10^{-4}$

S-6 Because of the relationship between the linear L scale and the C and D scales, one must conclude that the C, D scales are logarithmic scales. Note that the linear distance between the numbers one and two on the D scale is much greater than the linear distance between the numbers three and four. To multiply two numbers by slide rule, add a portion of the logarithmic C scale to the logarithmic D scale. For example, to multiply 2 x 3, add two log units of the C scale to three log units of the D scale:



The sum of this addition is read on the D scale directly below the 2 on the C scale.

Q-9 Using your slide rule, multiply the following

a) 1.50 x 3.0 b) 3.1 x 2.1

A-9 a) 4.5 b) 6.5

Q-10 Using your slide rule, multiply the following

a) 3.8 x 2.1 b) 2.11 x 4.0

A-10 a) 8.0 b) 8.4

Q-11 Using your slide rule, multiply the following

a) 4.5 x 1.2 b) 1.8 x 3.7

A-11 a) 5.4 b) 6.7

S-7 What happens if larger numbers are multiplied, for example (2 x 6)? If the left index line of the C scale is set at 6 on the D scale, the number 2 on the C scale is beyond the end of the D scale. This is because the D scale reads from one to ten and the product of 6 x 2 is 12 which is greater than ten. If an additional D scale could be added to the right of the one on the rule, then the answer could be read directly because the added D scale would read from ten to one hundred. The same thing can be accomplished, however, by placing the <u>right</u> hand index line of the C scale on the number 6 of the D scale and placing the hairline on the number 2 of the C scale. The answer twelve is then read on the D scale.

Q-12 Using your slide rule, multiply the following.

a) 5.0 x 3.0 b) 6.0 x 7.0

A-12 a) 15 b) 42

Q-13 Using your slide rule, multiply the following.

a) 9.30 x 7.00 b) 8.10 x 3.20

A-13 a) 65.1 b) 25.9

Q-14 Using your slide rule, multiply the following.

a) 8.50 x 6.80 b) 5.45 x 6.35

A-14 a) 57.8 b) 34.6

S-8 Very large numbers can be multiplied on the slide rule by first rewriting them in scientific notation. The unit number portion of the number is then multiplied as before. Thus, 3,280 x 462 becomes $3.280 \times 10^3 \times 4.62 \times 10^2$, and the answer found on the slide rule is 152. Knowing that 3 x 4 is 12, the correct answer for 3.28 x 4.62 must be 15.2. Multiplying the exponential numbers, $10^3 \times 10^2$, gives the final answer of 15.2×10^5. In summary then, to multiply very large (or small) numbers, the numbers are expressed in scientific notation; then the unit numbers are multiplied on the slide rule and the powers of ten are added. (The slide rule does not give the location of the decimal point in the answer.)

Q-15 Using your slide rule, multiply the following.

a) 3 970 x 97.2 b) 0.0124 x 58 2

A-15 a) 3 86 x 10^2 b) 7 22 x 10^{-1}

Q-16 Using your slide rule, multiply the following.

a) 422 x 89, 500 b) 0.00218 x 0.00312

A-16 a) 3 77 x 10^7 b) 6.80 x 10^{-6}

R To multiply numbers, logs are added. The C and D scales are log scales.

S-9 To divide two numbers, logarithms are subtracted. Therefore, to divide two numbers on the slide rule, the number on the C scale is subtracted from the number on the D scale, i.e., the divisor on the C scale is subtracted from the dividend on the D scale. Consider first a division in which the divisor is smaller than the dividend, e.g., 28/2.0. Set the hairline on the 28 of the D scale Subtract the log of 2.0 from this number by placing the 2 of the C scale under the hairline (the 2 should be directly above the 28) Read the answer 14 on the D scale directly below the left hand index line of the C scale

Q-17 Using your slide rule, divide the following.

a) 32/2.0 b) 49.6/4.10

A-17 a) 16 b) 12.1

Q-18 Using your slide rule, divide the following.

a) 78.2/3.00 b) 57.4/1.50

A-18 a) 26.1 b) 38.3

S-10 Now consider a division in which the divisor is larger than the dividend, e.g., 8.0/9.0. When the hairline is placed over the 8 on the D scale and the 9 of the C scale is placed under the hairline (the 9 should be directly above the 8), the left hand index line on the C scale is beyond the end of the D scale. The right hand index line of the C scale, however, is on the D scale at 890. The answer must be slightly less than one (8/9 is less than one) so the correct answer must be 0.89.

Q-19 Using your slide rule, divide the following.

a) 87/9.0 b) 6.1/9.54

A-19 a) 9.7 b) 0.64

Q-20 Divide the following.

a) 13.4/8.70 b) 91.4/97.6

A-20 a) 1.54 b) 0.936

S-11 To divide very large (or small) numbers, first express the numbers in scientific notation, then divide the unit numbers and subtract the exponents. For example

$$\frac{9,380}{0.00712} = \frac{9.38 \times 10^{3}}{7.12 \times 10^{-3}} = 1.32 \text{ (from slide rule)} \times 10^{6}$$

Q-21 Divide the following

a) 43,800/32,600 b) 0.0570/9,321

A-21 a) 1.34×10^{0} b) 6.12×10^{-6}

Q-22 Divide the following.

a) $97,200/6.02 \times 10^{23}$
b) 0.000320/0.00872

A-22 a) 1.61×10^{-19} b) 3.67×10^{-2}

S-12 In many problems, there will be a series of multiplications and divisions to carry out. The quickest way to carry out such a process is 1) divide, 2) multiply, 3) divide, 4) multiply, etc For example·

$$\begin{array}{c|c} 32.2 & 2.00 \\ \hline 0.1021 & 187.0 \end{array}$$

1) divide 32.2/0.1021 and find the answer below the left hand index line of the C scale,
2) multiply the answer in 1) by 2.00 by placing the hairline on the number 2 of the C scale (the answer to this should be 630);
3) divide the answer to 2) (630) by 187.0 by placing 187 under the hairline (187 should be directly above 630);
4) this completes the operations, and as the last process was a division, the answer is found under the left hand index line of the C scale (337)

To determine the proper position of the decimal point, approximate the answer, e.g.:

1) $32.2/0.1021 \approx 320$
2) $320 \times 2 = 640$
3) $640/187 \approx 2$ or 3

Therefore, the answer must be 3.37.

Q-23 Carry out the following operations.

a) $\begin{array}{c|c} 32.4 & 97.2 \\ \hline & 81.0 \end{array}$ b) $\begin{array}{c|c} 9.72 & 87.0 \\ \hline 0.312 & 42.3 \end{array}$

A-23 a) 38.9 b) 64.1

Q-24 Carry out the following operations.

a) $\begin{array}{c|c} 54.8 & 48.2 \\ \hline & 0.107 \end{array}$ b) $\begin{array}{c|c} 0.103 & 67.2 \\ \hline 81.0 & 4.10 \end{array}$

A-24 a) 2.47×10^{4} b) 2.08×10^{-2}

Q-25 Carry out the following operations.

a) $\begin{array}{c|c|c} 38.1 & 740 & 273 \\ \hline & 760 & 301 \end{array}$

b) $\begin{array}{c|c|c} 560 & 8.01 & 0.781 \\ \hline & 6.02 \times 10^{23} & 3.33 \end{array}$

A-25 a) 33 6 b) 1.75×10^{-21}

Q-26 Carry out the following operations.

a)

48 1	976	0.103
1.80	482	0.0078

b)

0 190	2 00	8.00	1000	
28.6	261 2	2 00	1 00	2 00

A-26 a) 715 b) 0.102

Q-27 Carry out the following operations.

a)

0.762	1000	273	760
28 2	1.00	299	1400

b)

0 333	8 21	4760	990	76.0
	47 6	93 8	4.20	221

A-27 a) 13 4 b) $2\ 36 \times 10^2$

S-13 Square roots are determined by dividing the log of a number by two. On the slide rule, the A and D scales are used to find square roots. Find the A scale. Note that it is a two cycle log scale, that is, it has two log scales end to end The first log scale runs from 1 to 10 while the second log scale runs from 10 to 100 Each unit on the A scale is exactly one half as long as the corresponding unit on the D scale. That is, the distance in cm between the two and three on the A scale is just half the distance (in cm) between the two and three on the D scale. Thus, if a distance is measured on the A scale but read on the D scale, it is equivalent to dividing the original distance by two. Place the hairline of your slide rule on 9 of the A scale Now read the square root of 9 on the D scale. To square a number, the reverse process is used To square four (4^2) place the hairline on the 4 of the D scale and read the answer on the A scale.

Q-28 Using your slide rule, find the square root of.

a) 4.0 b) 6.0

A-28 a) 2.0 b) 2.45

Q-29 Using your slide rule, find the square root of:

a) 8.50 b) 3.82

A-29 a) 2.92 b) 1.95

Q-30 Using your slide rule, find the square root of:

a) 12.2 b) 15.2

A-30 a) 3 48 b) 3.90

Q-31 Using your slide rule, find the square root of:

a) 22.2 b) 30.0

A-31 a) 4.71 b) 5.47

Q-32 Using your slide rule, find the value.for:

a) $(6.0)^2$ b) $(7.2)^2$

A-32 a) 36 b) 52

Q-33 Using your slide rule, find the value for:

a) $(2.3)^2$ b) $(1.95)^2$

A-33 a) 5.3 b) 3.80

S-14 To find square roots of numbers which do not fall within the range one to one hundred, e.g., 127, express the number exponentially in such a way that the numerical portion of the number lies between one and one hundred and that the exponent is an even number. For 127, express the number as 1.27×10^2 (not as 12.7×10^1, for even though 12.7 is between 1 and 100, the exponent is odd). Next find the square root of 1.27 on the slide rule and divide the exponent by the degree of the root.

$$\sqrt[2]{1.27 \times 10^2} = 1.13 \times 10^1$$

Q-34 Using your slide rule, find the square root of:

a) 181 b) 9720

A-34 a) 13.5 b) 98.6

Q-35 Using your slide rule, find the square root of:

a) 0.00310 b) 0.0762

A-35 a) 5.57×10^{-2} b) 0.276

Q-36 Using your slide rule, find the square root of

a) 49,700 b) 6.02×10^{23}

A-36 a) 2.23×10^2 b) 7.76×10^{11}

S-15 To square a number, merely reverse the process of finding the square root. For example, to square 4, set the hairline on 4 of the D scale and read the answer 16 on the second cycle of the A scale. For numbers greater than ten or less than one, express the number in scientific notation, then square the unit number on the slide rule and double the power of ten:

$$\begin{aligned} 1020^2 &= (1.02 \times 10^3)^2 \\ &= 1.04 \text{ (from slide rule)} \times 10^6 \\ 0.00831^2 &= (8.31 \times 10^{-3})^2 \\ &= 69.1 \text{ (from slide rule)} \times 10^{-6} \end{aligned}$$

Q-37 Using the slide rule, square the following numbers.

a) 5.0 b) 9.0

A-37 a) 25 b) 81

Q-38 Using the slide rule, square the following numbers.

a) 4.22 b) 3.10

A-38 a) 17.8 b) 9.61

Q-39 Using the slide rule, square the following numbers.

a) 43.0 b) 96.6

A-39 a) 18.5×10^2 b) 93.3×10^2

Q-40 Using the slide rule, square the following numbers.

a) 0.0810 b) 0.123

A-40 a) $65\ 6 \times 10^{-4}$ b) $1\ 51 \times 10^{-2}$

Q-41 Using the slide rule, square the following numbers.

a) 14,200 b) 760

A-41 a) $2\ 02 \times 10^{8}$ b) $57\ 8 \times 10^{4}$

Q-42 Using the slide rule, square the following numbers.

a) 0 0000131 b) 0.000457

A-42 a) $1\ 72 \times 10^{-10}$ b) $20\ 9 \times 10^{-8}$

S-16 To find the cube root of a number, the log of the number must be divided by three. On the slide rule, the K scale is a three cycle log scale. The first cycle goes from one to ten, the second from ten to one hundred, and the third from one hundred to one thousand. Each linear unit on the K scale is exactly one third a linear unit on the D scale, i. e., the distance in cm between the two and three on the K scale is exactly one third the distance in cm between the two and three on the D scale When the hairline is on the number 8 of the K scale (first cycle), the cube root will be under the hairline on the D scale (2). To find the cube root of 27, place the hairline on the 27 of the K scale (second cycle) and find the number 3 beneath the hairline on the D scale To find the cube root of the number 125, place the hairline on the 125 of the K scale (third cycle) and find the number 5 beneath the hairline on the D scale. To find the cube roots of numbers larger than 1000 or smaller than 1, express the number exponentially so that the numerical portion is between 1 and 1000 and the exponent of 10 is a multiple of 3. Then find the cube root of the numerical portion from the slide rule and divide the exponent by three For example, to find the cube root of 1270, first express it as 1.270×10^{3} (not as 12.70×10^{2} or $127\ 0 \times 10^{1}$ because the exponent is not a multiple of 3). Find the cube root of 1.27 (1 08) and divide the exponent by 3. The answer is 1.08×10^{1}.

Q-43 Using your slide rule, find the cube root of.

a) 12.7 b) 932

A-43 a) 2.33 b) 9 77

Q-44 Using your slide rule, find the cube root of:

a) 1.51 b) 631

A-44 a) 1.147 b) 8.58

Q-45 Using your slide rule, find the cube root of:

a) 4020 b) 98,000

A-45 a) 15.90 b) 46.0

Q-46 Using your slide rule, find the cube root of:

a) 0.0033 b) 0.000067

A-46 a) 0.1488 b) 0.0406

Q-47 Using your slide rule, find the cube root of:

$$2.3 \times 10^{-4}$$

A-47 $2.3 \times 10^{-4} = 230 \times 10^{-6}$

$(230 \times 10^{-6})^{\frac{1}{3}} = 6.13 \times 10^{-2}$

S-17 To cube a number, reverse the process of finding cube roots. To cube 6, for example, set the hairline on 6 of the D scale and read the answer, 216, on the third cycle of the K scale. To cube numbers larger than ten or less than one, express the number exponentially, cube the numerical portion and multiply the exponent by 3. For example

$$(0.0031)^3 = (3.1 \times 10^{-3})^3$$
$$= 29.8 \text{ (from slide rule)} \times 10^{-9}$$

	Q-48 Using your slide rule, cube the following numbers a) 3.80 b) 6.20
A-48 a) 54.9 b) 240	Q-49 Using your slide rule, cube the following numbers. a) 31.2 b) 15,200
A-49 a) 30.4×10^3 b) 3.51×10^{12}	Q-50 Using your slide rule, cube the following numbers a) 0.0230 b) 0.0000720
A-50 a) 1.22×10^{-5} b) 3.73×10^{-13}	Q-51 Using your slide rule, carry out the indicated operations a) $(0.0022)^{\frac{1}{3}}$ b) $(97{,}600)^{\frac{1}{2}}$
A-51 a) 0.13 b) 312.4	Q-52 Carry out the indicated operations. a) $(23.20)^2$ b) $\sqrt[2]{0.00321}$
A-52 a) 538 b) 0.0566	Q-53 Carry out the indicated operations. a) $\sqrt[2]{9.76 \times 10^{-23}}$ b) $(4{,}320)^{\frac{1}{3}}$
A-53 a) 9.88×10^{-12} b) 16.29	Q-54 Carry out the indicated operations. a) $(97{,}000{,}000)^3$ b) $(0.0421)^2$
A-54 a) 9.13×10^{23} b) 0.00177	Q-55 Carry out the indicated operations. a) $(0.00361)^3$ b) $\sqrt[2]{56{,}000}$
A-55 a) 4.70×10^{-8} b) 236.6	Q-56 Carry out the indicated operations. a) $(42{,}500)^2$ b) $(0.000078)^2$
A-56 a) 1.806×10^9 b) 6.08×10^{-9}	Q-57 Carry out the indicated operations. a) $(4{,}580)^3$ b) $(0.000280)^3$
A-57 a) 9.607×10^{10} b) 2.19×10^{-11}	Q-58 Carry out the indicated operations. a) $(56{,}200)^{\frac{1}{3}}$ b) $(0.00000120)^{\frac{1}{3}}$

A-58 a) 38.30 b) 0 0106

Q-59 Carry out the indicated operations

a) log 10 21 b) antilog 2 312

A-59 a) 0 0090 + 1 = 1.0090
b) 205

Q-60 Carry out the indicated operations

a) log 0.00231 b) antilog -2 731

A-60 a) 0 364 - 3 = -2 636
b) 0 001858

R **Do not try to memorize what scales are used for a particular operation. Find the proper scales and procedure by solving a simple problem (e.g., 2 x 4, 8/2, 4^2, $9^{1/2}$, $27^{1/3}$).**

PART III: Treatment of Experimental Data

S-1 Accuracy is a term used to express the difference between a measured value and the true value. Precision is a term used to express the difference between a measured value and the average value for a series of measurements. For example, consider the results obtained by three students for the % cobalt in a chemical sample.

Student A	Student B	Student C
10 19	18.56	15.60
10 21	18.55	18.72
10 20	18 58	5.68
10 22	18 58	4.24

If the true value is 10 20, then Student A obtained accurate and precise results, Student B obtained inaccurate but precise results, and Student C obtained neither accurate nor precise results. It is important to recognize that all measurements are inaccurate to some degree. The numbers which are used to report measurements should reflect the reliability of the measured values and the results from calculations should reflect the precision of the measurements Thus, if one uses a buret graduated in milliliters with 0.10 ml subdivisions, one can estimate reliably to 0.02 ml by interpolation. It would be legitimate to report a reading from such an instrument as 10 52 ml, but foolhardy to report the reading is 10.522 ml. All numbers which are known reasonably well are said to be significant figures. Thus, the buret reading, 10 52, has four significant figures, the last digit (2) having a greater uncertainty than the other digits. Note that the decimal point does not determine the number of significant figures.

Q-1 How many significant figures are there in the following numbers?

a) 100.21
b) 32.275
c) 0.872

A-1 a) 5 b) 5 c) 3

Q-2 In each number, indicate the digit known with the least reliability.

a) 1028.1 b) 0.07322

A-2 a) 1028 $\underline{1}$ b) 0 0732$\underline{2}$

Q-3 In each number, indicate the digit known with the least reliability.

a) 9 37 b) 1.23×10^{12}

A-3 a) 9 3$\underline{7}$ b) $1.2\underline{3} \times 10^{12}$

S-2 There are several general rules governing the significance of zeros:

a) $\underline{\text{final}}$ zeros $\underline{\text{after}}$ a decimal point are significant figures,
b) $\underline{\text{final}}$ zeros $\underline{\text{before}}$ a decimal point may or may not be significant, e.g., 10,000 may have from one to four significant figures, the best practice for such numbers is to express them exponentially with the numerical portion giving the number of significant figures. For example, to express ten thousand with three significant figures, it should be written 1.00×10^4,
c) if a number is $\underline{\text{less}}$ than one, zeros following the decimal point are not significant but those following the digits would be, e.g.,

$$\underbrace{0.00}_{\text{not significant}}123\underbrace{00}_{\text{significant}}$$

Q-4 Express the following to three significant figures

a) one hundred fifty thousand
b) ten grams
c) one thousandth of a cm

A-4 a) 1.50×10^5
b) 10.0 g
c) 0.00100 cm or 1.00×10^{-3} cm

Q-5 How many significant figures are shown in each of the following?

a) 0.00321 b) 0.070

A-5 a) 3 b) 2

Q-6 How many significant figures are shown in each of the following?

a) 10.0 b) 100

A-6 a) 3 b) do not know

Q-7 How many significant figures are shown in each of the following?

a) 1.230×10^{14} b) 1.02

A-7 a) 4
b) 3 (the zero after the decimal is significant as the number is greater than one.)

S-3 When rounding off a number follow these rules

a) when a number less than five is dropped, the last remaining digit is left unchanged,
b) when a number more than five is dropped, the last remaining digit is increased by one,
c) when the number five is dropped and the last remaining digit is even, no change is made in this digit, if the last remaining digit is odd, then it is increased by one. For example

9 375 rounded to 9 38
9 365 rounded to 9 36

	Q-8 Round off the following to four significant figures. a) 19.223 b) 27.897
A-8 a) 19.22 b) 27 90	Q-9 Round off the following to four significant figures. a) 0.13752 b) 0.29998
A-9 a) 0.1375 b) 0 3000	Q-10 Round off the following to four significant figures. a) 14 215 b) 29.385
A-10 a) 14.22 b) 29.38	

S-4 Numerical answers resulting from calculations cannot be more precise than the data used in the calculations. Thus, if the numbers 123 and 0.17 were added, the answer 123.17 would suggest that the quantity is known with reasonable accuracy to ± 1 unit in the hundredths place. Yet the number 123 is uncertain by 1 unit in the units place so that the digits 0.17 have no meaning. If we multiply 1.5 x 0.7, the answer is 1.05. This answer suggests three significant figures, yet the one piece of data (0.7) is known only to one significant figure. The rule to follow in addition and subtraction is:

a) round off the sum or difference to the largest place with uncertainty, e.g.,

$$\begin{array}{r} 10.789 \\ -\ 1.6 \\ \hline 9.189 \end{array}$$

but the largest place with a degree of uncertainty is the tenths place. Therefore, the answer is rounded off to 9.2.

The rule to follow in multiplication and division is:

b) the final result should contain the same number of significant figures as that number in the calculations which has the fewest number of significant figures, e.g.,

$$\frac{3202}{2.0} = 1601$$

but the divisor has only two significant figures, therefore, the answer must be reported as 1.6×10^3 or 16×10^2; (15.0)(3001)(3.1) = 13954.65 but the fewest number of significant figures in any single number used in the calculations was two (3.1) so the answer must be expressed as 1.4×10^4 or 14×10^3.

Q-11 Carry out the following process and give the answer to the correct number of significant figures

a) $$\begin{array}{r} 10.375 \\ \underline{+1.23} \end{array}$$

b) $(10 \times 10^4) + 123 + 1,420$

A-11 a) 11.605 rounded off to the hundredths place = 11.60

b) the original answer of 101,543 must be rounded off to the ten thousand place; 100,000 or 10×10^4 is the correct answer.

Q-12 Carry out the following process and give the answer to the correct number of significant figures

a) $$\begin{array}{r} 17.321 \\ \underline{-16} \end{array}$$

b) $$\begin{array}{r} 2194.22 \\ \underline{-1.001} \end{array}$$

A-12 a) 1.321 rounded off to the unit place = 1

b) 2193.219 rounded off to the hundredth place = 2193.22

Q-13 Carry out the following process and give the answer to the correct number of significant figures.

a) $$\frac{(37.8)(407.6)}{3.1}$$

b) $$\begin{array}{c|c|c} 760.0 & 22.4 & 18.6 \\ \hline 740.0 & 1000.0 & \end{array}$$

A-13 a) 4970.09032 rounded off to 5.0×10^3 because 3.1 has the least (two) number of significant figures.

b) 0.4278976 rounded off to 0.428 because three significant figures are the least number of significant figures in any number used.

Q-14 Find the average of the following.

$$\begin{array}{r} 18.75 \\ 19.63 \\ 17.48 \\ 19.0 \\ \underline{18.31} \end{array}$$

A-14 $\frac{93.17}{5.0000} = 18.634$

but one number (19.0) has uncertainty in the tenths place; therefore, we must round off the sum of the numbers to the tenths place, i.e., 93.2. The final answer can have only three significant figures and must be written as 18.6

Q-15 A certain substance weighed 1.0652 g and had a volume of 0.872 cm^3. What was the density of the substance in g/cm^3?

A-15 $\frac{1.0652\ g}{0.872\ cm^3} = 1.22156\ g/cm^3$

but one number (0.872) has only three significant figures, so the answer must be rounded off to 1.22.

Q-16 The density of a liquid was found by weighing a volume of the liquid measured from a buret. The initial buret reading was 0.02 ml. The final buret reading was 10.38 ml. The mass of the empty flask was 14.0731 g while the mass of the flask plus liquid was 22.9875 g. What is the density of the liquid in g/ml?

A-16 volume of liquid: mass of liquid

$$\begin{array}{r} 10.38 \\ -\ 0.02 \\ \hline 10.36 \text{ ml} \end{array} \qquad \begin{array}{r} 22.9875 \\ -14.0731 \\ \hline 8.9144 \text{ g} \end{array}$$

$$\text{density} = \frac{8.9144}{10.36} = 0.860463 \text{ g/ml}$$

However, one number used in the calculations has only four significant figures, therefore, the density must be given as 0.8605 g/ml.

S-5 The last digit in all answers is unreliable to some degree. But to determine how unreliable, i.e., to find the "right" answer, the scientist needs to make a large number of measurements of the same quantity. When the values of these measurements are plotted against the frequency with which the value was observed, a normal distribution curve (Fig. I) would result:

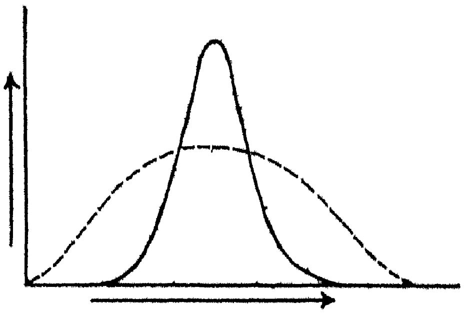


Figure I

Q-17 Which point on each of the two curves in Fig. I represents the most probable value of the "right" answer?

A-17 The highest point on each curve represents the most probable value of the right answer because these values are observed most often.

Q-18 Which curve in Fig. I reflects the more precise set of measurements?

A-18 The solid line curve represents the more precise set of measurements for it has a smaller range of observed values.

S-6 The breadth of the distribution curve gives a measure of the reliability of the measurements. One way of describing this breadth is by the average deviation. The average deviation is defined by the formula:

$$\frac{\Sigma\,|\bar{x} - x_i|}{n}$$

where Σ indicates a summation of the terms for all values of i, $\bar{x}$ is the average value of all the measurements, x_i is the value of the i^{th} measurement, and n is the total number of measurements. The deviations of the measured values from the average are summed up and then divided by the number of measurements. For example, the average deviation for the following set of values is computed thusly:

x_i	$\overline{x} - x_i$
10.20	0.06
10.11	0.15
10.31	0.05
10.41	0.15
10.26	0.00
10.36	0.10
10.18	0.08
71.83 $\quad n = 7$	0.59

n is an absolute number and can have any number of significant figures

$$\overline{x} = \frac{71.84}{7.000} = 10.26$$

$$\text{av. dev.} = \frac{\Sigma\,|\overline{x} - x_i|}{n} = \frac{0.59}{7.0} = 0.08$$

The answer should be expressed as 10.26 $\pm$ 0.08

Q-19 Find the average deviation of:

x_i
0.978
0.899
0.942
0.921
0.895
0.952

A-19 $\Sigma x_i = 5.587 \quad n = 6$ (absolute number with any number of significant figures)

$$\overline{x} = \frac{\Sigma x_i}{n} = 0.931$$

$$\text{av. dev.} = \frac{\Sigma|\overline{x} - x_i|}{n} = \frac{0.157}{6.00} = 0.026$$

This number must be rounded off to 0.026 because none of the data are accurate in the ten thousandths place.

Q-20 Find the average deviation for the following determinations of the population of a city taken by seven different census takers.

number of people
10,212
10,980
10,485
10,212
9,987
10,567
10,855

A-20

$\lvert\overline{x} - x_i\rvert$
259
509
14
259
484
96
384
2,005

$$\overline{x} = \frac{\Sigma x_i}{n} = \frac{73,298}{7} = 10,471$$

$$\text{av. dev.} = \frac{\Sigma|\overline{x} - x_i|}{n} = 286.4$$

This must be rounded off to 286 as none of the data is accurate in the tenths place.

S-7 While the average deviation is easy to calculate, it is not as good an estimate of reliability as the standard deviation The shape of the normal distribution curve (Fig. I, S-5) is related to the standard deviation The larger the standard deviation the more spread out is the curve The standard deviation is defined by the formula

$$S = \sqrt{\frac{\Sigma\,(\bar{x} - x_1)^2}{n - 1}}$$

where $\bar{x}$, x_1, and n are the same as defined for average deviation It is important to note that each difference is squared and these squared quantities are then summed. For example, to find the standard deviation for the following values, proceed as follows·

x_1	$\bar{x} - x_1$	$(\bar{x} - x_1)^2$
10 20	0.06	4×10^{-3}
10 11	0.15	22×10^{-3}
10 31	0.05	2×10^{-3}
10 41	0.15	22×10^{-3}
10 26	0.00	- - -
10 36	0.10	10×10^{-3}
10 18	0 08	6×10^{-3}
71 83 = Σx_1		66×10^{-3}

$\bar{x}$ = 10.26

$$S = \sqrt[2]{\frac{\Sigma\,(\bar{x} - x_1)^2}{n - 1}} = \sqrt[2]{\frac{0\ 066}{6.000}} = 0.11$$

Q-21 Which of the curves in Fig. I, S-5 represents the larger standard deviation?

A-21 The dashed curve.

Q-22 Find the standard deviation of the following quantities.

x_i
0.978
0.899
0.942
0.921
0.895
0.952

A-22 $\bar{x}$ = 0.931

$\bar{x} - x_1$	$(\bar{x} - x_i)^2$
0.047	22×10^{-4}
0 032	10×10^{-4}
0 011	1.2×10^{-4}
0.010	1.0×10^{-4}
0.036	13×10^{-4}
0.021	4.4×10^{-4}

$\Sigma\,(\bar{x} - x_i)^2 = 52 \times 10^{-4}$

$$S = \sqrt[2]{\frac{\Sigma\,(\bar{x} - x_i)^2}{n - 1}}$$

$$= \sqrt[2]{\frac{52 \times 10^{-4}}{5.00}} = 0.032$$

Q-23 Find the standard deviation for the following determinations of the population of a city taken by seven different census takers.

number of people
10,212
10,980
10,485
10,212
9,987
10,567
10,855

Compare the value of the standard deviation with the average deviation calculated in A-20.

A-23 $\bar{x} = \frac{\Sigma x_1}{n} = \frac{73,298}{7} = 10,470$

$\lvert \bar{x} - x_1 \rvert$	$(\bar{x} - x_1)^2$
259	6 71 x 10^4
509	25 9 x 10^4
14	0 02 x 10^4
259	6 71 x 10^4
484	23 4 x 10^4
96	0 92 x 10^4
384	14 7 x 10^4
	78 36 x 10^4 = 78.4 x 10^4

$$S = \sqrt{\frac{\Sigma(\bar{x} - x_1)^2}{n - 1}} = \sqrt{\frac{78\ 4 \times 10^4}{7 - 1}}$$

$$= \sqrt{13.1 \times 10^4} = 3.62 \times 10^2 = 362$$

Q-24 Method A for the determination of the percent iron in a sample gave the following results

% Fe
12 42
12 48
12.41
12 50
12 40

Calculate the standard deviation of the above results

A-24

% Fe	$\bar{x} - x_i$	$(\bar{x} - x_1)^2$
12 42	0 02	0 0004
12.48	0.04	0.002
12 41	0.03	0.0009
12.50	0.06	0 004
12.40	0.04	0.002
62.21		0 009

$$\bar{x} = \frac{62.21}{5} = 12.44$$

$$S = \sqrt{\frac{\Sigma(\bar{x} - x_i)^2}{n - 1}} = \sqrt{\frac{0.009}{4}} = \sqrt{0.002} = 0.04$$

Q-25 Method B for the determination of the percent iron in a sample gave the following results.

% Fe
10 00
12.90
12.98
9.90
13.50

Calculate the standard deviation of the above results.

A-25

% Fe	$\bar{x} - x_i$	$(\bar{x} - x_i)^2$
10.00	1.86	3.46
12.90	1.04	1.08
12.98	1.12	1.25
9.90	1.96	3.84
13.50	1.64	2.69
59.28		12.32

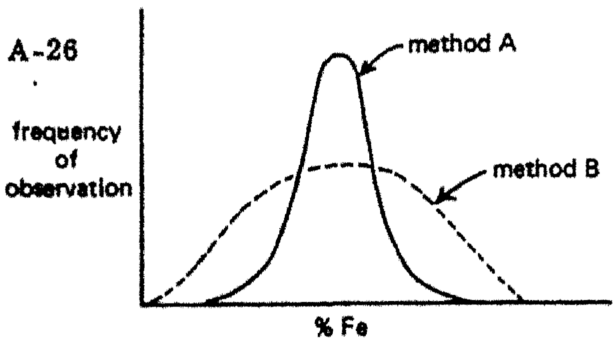
$$\bar{x} = \frac{59.28}{5} = 11.86$$

$$S = \sqrt{\frac{\Sigma(\bar{x} - x_i)^2}{n - 1}} = \sqrt{\frac{12.31}{4}} = \sqrt{3.08}$$

$$= 1.75$$

Q-26 Sketch the shape of the normal distribution curves for the determination of percent Fe by method A and method B

A-26



S-8 Many times it is convenient to analyze data by a graphic method. This is particularly true if the data can be represented by the equation

$$y = ax + c$$

where a and c are constants and y and x are experimentally determined quantities. It is obvious that a plot of y vs x should give a linear plot since the equation is that of a straight line function. If we wished to evaluate the constants a and c, we would first have to plot the data y vs x to find the slope of the line (which would be a) and the intercept (which would be c). The slope of the line is evaluated according to its mathematical definition:

$$a = \frac{y_2 - y_1}{x_2 - x_1}$$

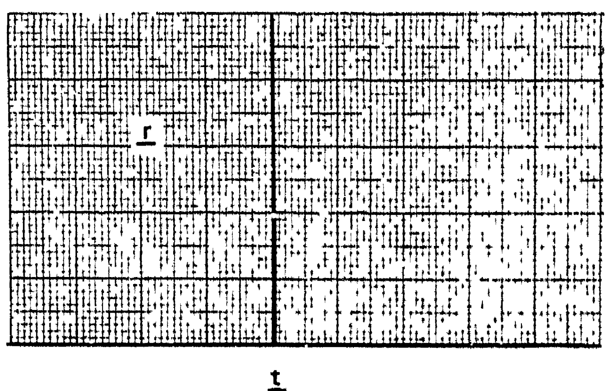
where (x_1, y_1) and (x_2, y_2) are any two points on the line. The intercept is simply that point where the line crosses the Y-axis (i. e., at x = 0).

Q-27 The functions r and t are related by the equation:

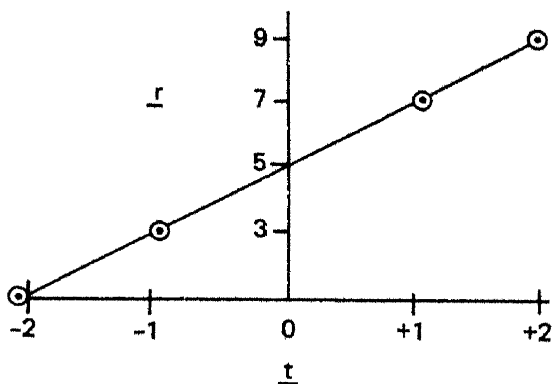
$$r = at. + c$$

For the following data, what is the value for the slope (a) and the intercept (c)?

r	t
1.00	-2.02
3.00	-0.98
7.00	+1.07
9.00	+1.97



A-27 First plot r vs. t:



The intercept is read directly off the graph as 4.95 or 5.0. The slope is determined according to the formula:

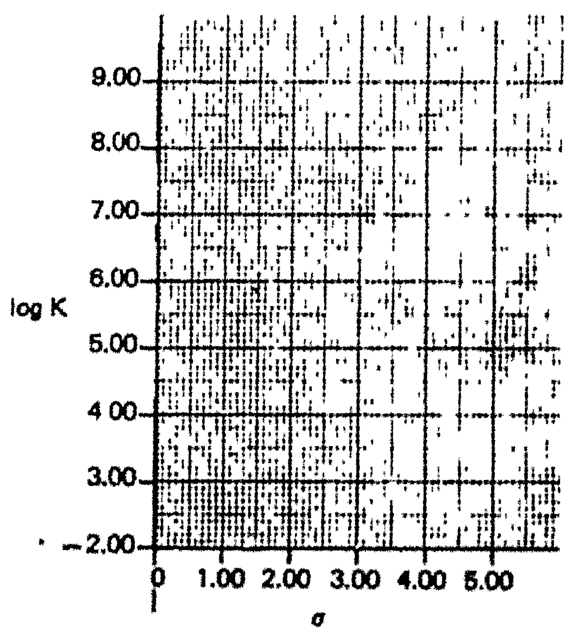
$$a = \frac{r_2 - r_1}{t_2 - t_1} = \frac{7.00 - 1.00}{1.07 - (-2.02)} = 1.94$$

Q-28 The experimental quantities K and σ are related by the equation:

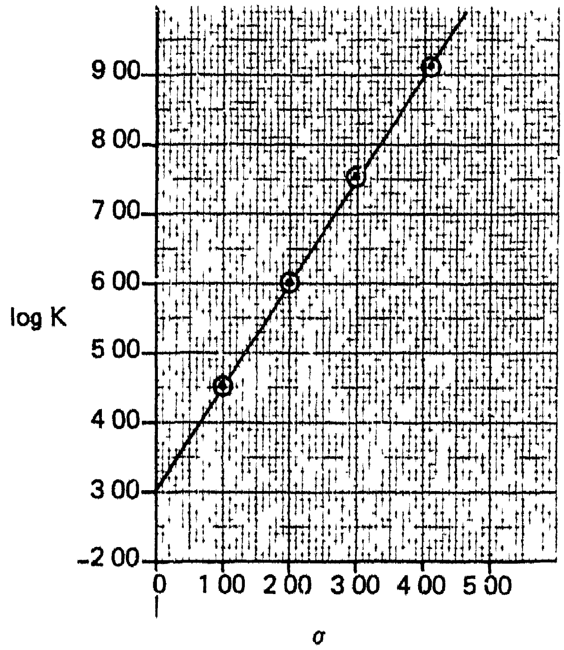
$$\log K = \rho\sigma + \log K°$$

where ρ and K° are constants. Plot the following data and determine the value of ρ and log K° from your graph

log K	σ
4.50	1.01
6.02	2.00
7.47	2.98
9.10	4.05



A-28 The plot of log K vs. σ should look like this



The slope of the line will be ρ and the intercept will be log K°. The intercept, as read directly from the graph is 3.0. The slope must be:

$$\rho = \frac{\log K_2 - \log K_1}{\sigma_2 - \sigma_1} = 1\ 5$$

S-9 Since the variables y and x in the equation in S-8 are experimental values, all the points will not lie on a single straight line, but will be scattered. The problem then becomes how to draw a line through these points so that the line represents the true values of the related function. One could draw, by visual approximation, a straight line falling as close as possible to all the points. However, as this is necessarily arbitrary and quite inaccurate, a better method would be a statistical one, such as the least mean square method. This method employs the principle that the most probable true value of an observed quantity is that value for which the sum of the squares of the deviations from it is at a minimum. Thus, for the straight line function:

$$y = ax + c$$

least mean squares enables us to evaluate the constants a (slope) and c (intercept) quite accurately. The slope is defined as:

$$a = \frac{q}{z}$$

where q is:

$$q = \Sigma(y \cdot x) - \frac{(\Sigma y)(\Sigma x)}{n}$$ (n is the total number of observations)

and z is:

$$z = \Sigma(x^2) - \frac{(\Sigma x)^2}{n}$$

The intercept is found from the equation:

$$c = \bar{y} - a\bar{x}$$

where $\bar{y}$ and $\bar{x}$ are the average values of y and x, respectively. For example, the slope and intercept of the following data is found by the least mean square method in the following way

y	y x	x	x^2
1 80	1 80	1 00	1.00
3 90	11 7	3 00	9.00
4 30	25 8	6 00	36.0
5 70	42 7	7 50	56.2
7 30	73 0	10 00	100.0
23 00	155 0	27.50	202.2

Having set up a table of the computed values required in this method, the values may then be substituted into the equations for slope and intercept. To find the slope, divide q by z:

$$q = \Sigma(y\ x) - \frac{(\Sigma y)(\Sigma x)}{n} = 155.0 - \frac{(23\ 00)(27.50)}{5} = 155.0 - 126.5 = 28.5$$

$$z = \Sigma(x^2) - \frac{(\Sigma x)^2}{n} = 202\ 2 - \frac{(27.50)^2}{5} = 202.2 - 151.2 = 51.0$$

$$a = q/z = \frac{28.5}{51\ 0} = 0\ 559$$

To find the intercept, first find $\bar{y}$ and $\bar{x}$:

$$\bar{y} = \frac{23\ 00}{5} = 4.60 \qquad \bar{x} = \frac{27\ 50}{5} = 5\ 50$$

$$\text{intercept (c)} = \bar{y} - a\bar{x} = 4\ 60 - (0.559)(5.50)$$

$$= 4.60 - 3.07 = 1.53$$

Substituting for a and c in the equation, $y = ax + c$, gives

$$y = (0.559)x + 1.53$$

Q-29 By use of the least square method, find the slope and intercept of the equation:

$$\log K = \rho\sigma + \log K^{\circ}$$

if the experimental values of σ and log K are as follows:

log K	σ
4.49	1.01
6.02	2.00
7.47	2.98
9.10	4.05

(Hint: first complete the table by finding (log K) (σ) and σ^2; then evaluate q and z; finally, find slope q/z and intercept.)

A-29 First complete the table

log K	(log K)(σ)	σ	σ^2
4 49	4. 54	1 01	1 02
6.02	12 04	2 00	4 00
7.47	22. 26	2 98	8 88
9 10	36 86	4 05	16 40
27.08	75. 70	10 04	30 30

Now to find the slope, evaluate q/z

$$q = \Sigma (\log K)(\sigma) - \frac{(\Sigma \log K)(\sigma)}{n}$$

$$= 75.70 - \frac{(27\ 09)(10\ 04)}{4}$$

$$= 7\ 70$$

$$z = \Sigma \sigma^2 - \frac{(\Sigma \sigma)^2}{n}$$

$$= 30.30 - \frac{(10.04)^2}{4}$$

$$= 5.10$$

$$\frac{q}{z} = \frac{7\ 70}{5\ 10} = 1\ 51$$

$$\text{intercept (c)} = \overline{\log K} - \rho\bar{\sigma}$$

$$= \frac{27\ 08}{4} - 1.51\ \frac{(10\ 04)}{4}$$

$$= 2.98$$

S-10 Several other important statistical values can be obtained from the squares method. The correlation coefficient gives an estimate of how well the data correlates to the straight line defined by the least mean squares method. Thus, if all our points fall exactly on the line, the correlation coefficient will be one. If the points are completely random on our graph, the correlation coefficient will be zero.

The correlation coefficient (c. c.) is defined as.

$$\text{c.c.} = \sqrt[2]{\frac{(q)^2}{(z)(w)}}$$

where q and z have the same values as before and for the equation, y = ax + c, w is defined as:

$$w = \Sigma y^2 - \frac{(\Sigma y)^2}{n}$$

Consider the data given in S-9. To find the correlation coefficient, the values for q, z, and w need to be computed. In S-9 q and z were evaluated. To find the value of w, Σy^2 and $(\Sigma y)^2$ must be determined first.

y	y^2
1.80	3.24
3.90	15.2
4.30	18.5
5.70	32.5
7.30	53.3
23.00	122.7

$$w = 122.7 - \frac{(23.00)^2}{5}$$

$$= 122.7 - 105.8 = 16.9$$

$$\text{c.c.} = \sqrt{\frac{(28.5)^2}{(51.0)(16.9)}} = \sqrt{\frac{812}{862}} = \sqrt{0.942} = 0.97$$

The correlation coefficient of 0.97 indicates that the experimental points fall very close to the line.

Q-30 Find the correlation coefficient for the data given in Q-29. (Hint: first determine $\Sigma \log K$ and $\Sigma (\log K)^2$, then evaluate w.)

A-30 q = 7 70 z = 5.10

To compute w, find $\Sigma (\log K)^2$.

log K	$(\log K)^2$
4.49	20 2
6 02	36 2
7 47	55.8
9.10	82.8
27 08	195.0

$$w = \Sigma (\log K)^2 - \frac{(\Sigma \log K)^2}{n}$$

$$= 195\ 0 - \frac{(27.08)^2}{4}$$

$$= 11.7$$

$$c.c. = \sqrt[2]{\frac{(7.70)^2}{(5.10)(11\ 7)}} = 0.99$$

S-11 Other interesting bits of information which can easily be computed from the data include the standard deviation of points from the line defined by least squares and the standard deviation of the slope of the line For example, consider Fig. II:

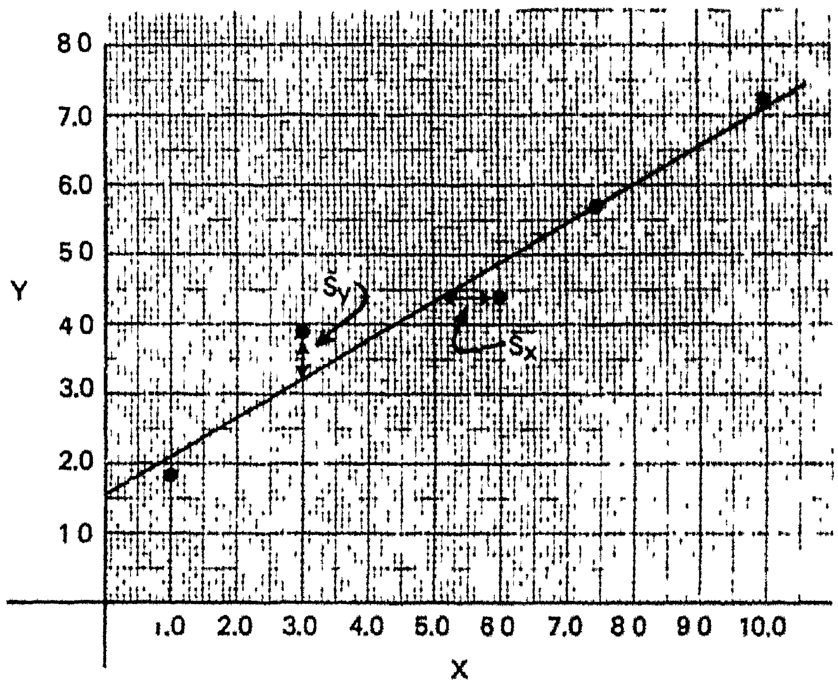


Figure II

The standard deviation of points from the line along the Y-axis (S_y) can be computed from the formula:

$$S_y = \sqrt[2]{\frac{w - \frac{q^2}{z}}{n - 2}}$$

Similarly, the standard deviation of points along the X-axis (S_x) can be computed from the formula

$$S_x = \sqrt[2]{\frac{z - \frac{q^2}{w}}{n - 2}}$$

The standard deviation of the slope is

$$S_a = \frac{S_y}{\sqrt[2]{z}}$$

From the information given in S-9 and S-10, the quantities q, z, and w had the values:

$$q = 28.5 \qquad z = 51.0 \qquad w = 16.9$$

Therefore,

$$S_y = \sqrt{\frac{16.9 - \frac{(28.5)^2}{51.0}}{5-2}} = 0.58 \qquad S_x = \sqrt{\frac{51.0 - \frac{(28.5)^2}{16.9}}{5-2}} = 1.0$$

$$S_a = \frac{S_y}{\sqrt{z}} = \frac{0.58}{\sqrt{51.0}} = \frac{0.58}{7.14} = 0.081 = 8.1 \times 10^{-2}$$

Q-31 Calculate S_x, S_y and S_a for the data given in Q-29.

A-31 $q = 7.70, \quad z = 5.10; \quad w = 11.7$

$$S_x = \sqrt[2]{\frac{5.10 - \frac{(7.70)^2}{11.7}}{4 - 2}} = 0.1$$

$$S_y = \sqrt[2]{\frac{11.7 - \frac{(7.70)^2}{5.10}}{4 - 2}} = 0.2$$

$$S_a = \frac{0.2}{5.10} = 0.1$$

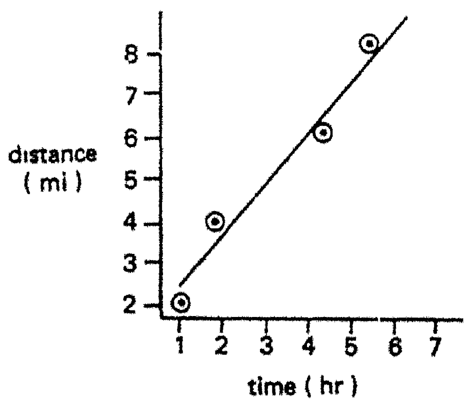
$$= \frac{0.2}{\sqrt{5.10}} = 0.1$$

Q-32 For the following data, make a plot and determine these quantities: slope, intercept, correlation coefficient, S_x, S_y, S_a. Use the least squares method for all calculations

d distance (mi)	t time (hr)
2.0	1.2
4.0	1.8
6.0	4.4
8.0	5.8

(Hint: first prepare a table of d^2, $d \cdot t$, and t^2.)

A-32



The first thing to do in the least squares determination is to complete the table:

d^2	d	$d \cdot t$	t	t^2
4	2.0	2.4	1.2	1.4
16	4.0	7.2	1.8	3.2
36	6.0	26	4.4	19
64	8.0	46	5.8	34
120	20.0	82	13.2	58

Next evaluate q, z, and w

$$q = 82 - \frac{(20\ 0)(13\ 2)}{4.00} = 16$$

$$z = 58 - \frac{(13\ 2)^2}{4} = 14$$

$$w = 120 - \frac{(20)^2}{4} = 20$$

$$\text{slope} = \frac{q}{z} = \frac{16}{14} = 1\ 1 \text{ mi/hr (average velocity)}$$

$$\text{intercept} = \bar{d} - (\text{slope})(\bar{t})$$

$$= 5 - (1.1)(3\ 3) = 1.4 \text{ mi (distance at } t = 0)$$

$$\text{c.c} = \sqrt[2]{\frac{(16)^2}{(14)(20)}} = 0\ 96$$

$$S_x = \sqrt{\frac{14 - \frac{16^2}{20}}{2}} = 0.77 \text{ hr}$$

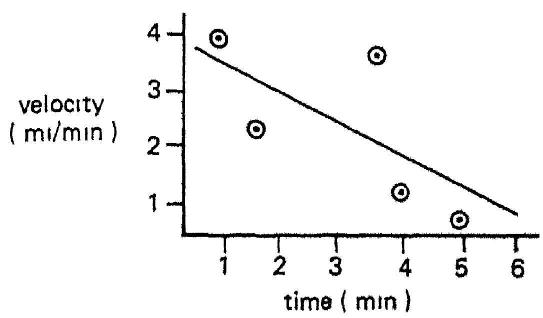
$$S_y = \sqrt{\frac{20 - \frac{16^2}{14}}{2}} = 0\ 92 \text{ mi}$$

$$S_a = \frac{S_y}{\sqrt[2]{14}} = 0\ 25 \text{ mi/hr}$$

Q-33 Make a plot for the following data and determine by the least squares method the slope, intercept, correlation coefficient, S_x, S_y, S_a

velocity (mile/min)	time (min)
3.90	1 00
2.25	1.50
3.65	3.50
1.25	4.00
0.60	5.00

A-33



The first thing to do in the least squares determination is to complete the table:

v^2	v	v·t	t	t^2
15 2	3.90	3.90	1.00	1.0
5.1	2.25	3.38	1.50	2.2
13.3	3.65	12.8	3.50	12.2
1 6	1 25	5.00	4.00	16.0
0 4	0.60	3.0	5.00	25.0
35.6	11.65	28.1	15 00	56.4

$\bar{v} = 2.33$ $\bar{t} = 3.00$

Then evaluate q, z, and w

$$q = 28.1 - \frac{(11.65)(15.00)}{5.00} = -6.9$$

$$z = 56.4 - \frac{(15.00)^2}{5.00} = 11.4$$

$$w = 35.6 - \frac{(11.65)^2}{5.00} = 8.5$$

$$\text{slope} = \frac{q}{z} = \frac{-6.9}{11.4} = -0.60 \text{ mi/min}^2 \text{ (deceleration)}$$

intercept = $\overline{v}$ - (slope)$\overline{(t)}$

= 2 33 -(-0 60)(3 00)

= 4.1 mi/min (velocity at t = 0)

$$c.c = \sqrt[2]{\frac{(-6.9)^2}{(11.4)(8.5)}} = \sqrt{0\ 49} = 0\ 70$$

$$S_x = \sqrt[2]{\frac{11.4 - \frac{(-6\ 9)^2}{8.5}}{3\ 00}} = 1.4 \text{ min}$$

$$S_y = \sqrt[2]{\frac{8.5 - \frac{(-6\ 9)^2}{11\ 4}}{3\ 00}} = 1.2 \text{ mi/min}$$

$$S_a = \frac{1.2}{\sqrt[2]{11.4}} = 0.35 \text{ mi/min}^2$$

All of the formulas necessary for computing least mean square quantities are [illegible]. It is not necessary to memorize these formulas, but you should know how to use [illegible]

equation: $r = at + c$

slope (a) $= \frac{q}{z}$; $q = \Sigma(r \cdot t) - \frac{(\Sigma r)(\Sigma t)}{n}$; $z = \Sigma t^2 - \frac{(\Sigma t)^2}{n}$

intercept (c) $= \overline{r} - a\overline{t}$; $\overline{r} = \frac{\Sigma r}{n}$; $\overline{t} = \frac{\Sigma t}{n}$

correlation coefficient (c.c.) $= \sqrt[2]{\frac{q^2}{(z)(w)}}$; $w = \Sigma r^2 - \frac{(\Sigma r)^2}{n}$

standard deviation along Y-axis [illegible] $= \sqrt{\frac{w - \frac{q^2}{z}}{n-2}}$

standard deviation along X-axis [illegible] $= \sqrt{\frac{z - \frac{q^2}{w}}{n-2}}$

standard deviation of slope [illegible]

PART IV: Units and the Unit Conversion Method

S-1 When reporting quantitative measurements of physical quantities it is essential to give the unit of measurement. Numbers by themselves have little meaning and it is necessary to add a unit to a numerical answer in order to make it useful. Besides being necessary to complete an answer, units are very helpful in the solution of a large number of problems encountered in all the natural sciences. This part of the programmed text will endeavor to teach how to solve certain types of problems by the Unit Conversion Method. The problems which you will be asked to do are not significant but the method of solving the problem is very significant. Even though you may be able to do some of these problems in your head, write out each answer using the Unit Conversion Method. The following conversion units should be committed to memory:

10^8 Angstroms (Å) = 1 cm	12 in = 1 ft	2000 lb = 1 T
10 mm = 1 cm	3 ft = 1 yd	454 g = 1 lb
100 cm = 1 meter	5280 ft = 1 mi	1000 g = 1 kg
2.54 cm = 1 in	16 oz = 1 lb	

The unit conversion method involves the multiplication of the starting data by a ratio that is equivalent to unity. This ratio is referred to as the unity factor. The unity factor must have a unit which will convert the unit of the starting data to a new unit. The unity factors are derived from known identities or equivalents. For example, since 1 mile = 5280 feet, the ratios 5280 ft/1 mile and 1 mile/5280 ft are equivalent to unity. To convert 10.0 miles to feet, multiply 10.0 miles by the unity factor, 5280 ft/1 mi, which will convert miles to feet

$$\frac{10.0\ \cancel{mi}}{} \Big| \frac{5280\ ft}{1\ \cancel{mi}} = 52800\ ft$$

Note that if 10.0 miles had been multiplied by the unity factor 1 mi/5280 ft, the units would not have cancelled

$$\frac{10.0\ mi}{} \Big| \frac{1\ mi}{5280\ ft} = \frac{10.0\ mi^2}{5280\ ft}$$

Q-1 Convert 16 in to cm.

A-1 Use the unity factor

$$\frac{2.54\ cm}{1\ in}$$

$$\frac{16\ \cancel{in}}{} \Big| \frac{2.54\ cm}{1\ \cancel{in}} = (16)(2.54)\ cm$$

Q-2 Convert 154 lb to oz.

A-2 Use the unity factor.

$$\frac{16\ oz}{1\ lb}$$

$$\frac{154\ \cancel{lb}}{} \Big| \frac{16\ oz}{1\ \cancel{lb}} = \frac{(154)(16)\ oz}{1}$$

Q-3 Convert 17 lb to g.

A-3 Use the unity factor:

$$\frac{454\ g}{1\ lb}$$

$$\frac{17\ \cancel{lb}}{} \Big| \frac{454\ g}{1\ \cancel{lb}} = \frac{(17)(454)\ g}{1}$$

S-2 Several steps may be necessary in order to develop the required unit in the answer. Thus to convert 16 mi to in the following unity factors must be used:

$$\frac{5280\ ft}{1\ mi} \quad \text{or} \quad \frac{1\ mi}{5280\ ft} \qquad \text{and} \qquad \frac{1\ ft}{12\ in} \quad \text{or} \quad \frac{12\ in}{1\ ft}$$

In each conversion, the unity factor is used that will cause the preceding units to be cancelled. The first conversion required is:

$$\frac{16\ \cancel{mi}}{} \Big| \frac{5280\ ft}{1\ \cancel{mi}} = \frac{(16)(5280)\ ft}{1}$$

while the second step is:

$$\frac{(16)(5280)\ \cancel{ft}}{} \Big| \frac{12\ in}{1\ \cancel{ft}} = \frac{(16)(5280)(12)\ in}{1}$$

These two steps can be done more conveniently as follows:

$$\frac{16\ \cancel{mi}}{} \Big| \frac{5280\ \cancel{ft}}{1\ \cancel{mi}} \Big| \frac{12\ in}{1\ \cancel{ft}} = \frac{(16)(5280)(12)\ in}{1}$$

Q-4 Convert 70 ft to cm

A-4 Use the unity factors

$$\frac{12 \text{ in}}{1 \text{ ft}} \text{ and } \frac{2.54 \text{ cm}}{1 \text{ in}}$$

$$\frac{70 \cancel{\text{ft}}}{} \left| \frac{12 \cancel{\text{in}}}{1 \cancel{\text{ft}}} \right| \frac{2.54 \text{ cm}}{1 \cancel{\text{in}}} = \frac{(70)(12)(2.54) \text{ cm}}{1}$$

Q-5 Convert 150 ft to Å.

A-5 Use the unity factors

$$\frac{12 \text{ in}}{1 \text{ ft}} \text{ and } \frac{2.54 \text{ cm}}{1 \text{ in}} \text{ and } \frac{1.0 \text{ Å}}{10^{-8} \text{ cm}}$$

$$\frac{150 \cancel{\text{ft}}}{} \left| \frac{12 \cancel{\text{in}}}{1 \cancel{\text{ft}}} \right| \frac{2.54 \cancel{\text{cm}}}{1 \cancel{\text{in}}} \left| \frac{1.0 \text{ Å}}{10^{-8} \cancel{\text{cm}}} \right.$$

$$= \frac{(150)(12)(2.54)(1.0) \text{ Å}}{1 \times 10^{-8}}$$

Q-6 Convert 12 yd^2 to meter^2

A-6 Use the unity factors

$$\frac{(36)^2 \text{ in}^2}{(1)^2 \text{ yd}^2} \text{ and } \frac{2.54^2 \text{ cm}^2}{1^2 \text{ in}^2} \text{ and } \frac{1^2 \text{ meter}^2}{(100)^2 \text{ cm}^2}$$

$$\frac{12 \cancel{\text{yd}^2}}{} \left| \frac{(36)^2 \cancel{\text{in}^2}}{1^2 \cancel{\text{yd}^2}} \right| \frac{(2.54)^2 \cancel{\text{cm}^2}}{1^2 \cancel{\text{in}^2}} \left| \frac{1^2 \text{ meter}^2}{(100)^2 \cancel{\text{cm}^2}} \right.$$

$$= \frac{(12)(36)^2(2.54)^2 \text{ meter}^2}{(100)^2}$$

Q-7 Find the mass of a piece of aluminum 3 in x 6.5 in x 1/8 in if the density of aluminum is 2.702 g per cm^3. (The chemical symbol for aluminum is Al.)

A-7 Use the unity factors.

$$\frac{(2.54)^3 \text{ cm}^3}{1^3 \text{ in}^3} \text{ and } \frac{2.702 \text{ g aluminum}}{1^3 \text{ cm}^3 \text{ aluminum}}$$

$$\frac{3 \times 6.5 \times 1/8 \cancel{\text{in}^3} \text{ aluminum}}{} \left| \frac{2.54^3 \cancel{\text{cm}^3} \text{ aluminum}}{1 \cancel{\text{in}^3} \text{ aluminum}} \right| \frac{2.702 \text{ g aluminum}}{1 \cancel{\text{cm}^3} \text{ aluminum}}$$

$$= (3)(6.5)(1/8)(2.54)^3(2.702) \text{ g aluminum}$$

Q-8 A car is traveling at a rate of 60 mi/hr. What is the rate of travel in Å per hour?

A-8

$$\frac{60 \cancel{\text{mi}}}{1 \text{ hr}} \left| \frac{5280 \cancel{\text{ft}}}{1 \cancel{\text{mi}}} \right| \frac{12 \cancel{\text{in}}}{1 \cancel{\text{ft}}} \left| \frac{2.54 \cancel{\text{cm}}}{1 \cancel{\text{in}}} \right| \frac{10^8 \text{ Å}}{1 \cancel{\text{cm}}}$$

$$\text{rate} = \frac{(60)(5280)(12)(2.54)(10^8) \text{Å}}{1 \text{ hr}}$$

Q-9 If a measuring worm traveled at the rate of 45 ft an hour, what was its rate of travel in ft/sec?

A-9 In this problem the denominator must be converted.

$$\frac{45 \text{ ft}}{1 \cancel{\text{hr}}} \left| \frac{1 \cancel{\text{hr}}}{60 \cancel{\text{min}}} \right| \frac{1 \cancel{\text{min}}}{60 \text{ sec}}$$

$$\text{rate} = \frac{45 \text{ ft}}{(60)(60) \text{ sec}}$$

Q-10 If a car travels at a rate of 30 mi/hr, what is its rate of travel in cm/sec? (Hint: convert the numerator from mi to cm, then convert the denominator from hr to sec.)

A-10 $$\frac{30\ \cancel{\text{mi}}}{1\ \cancel{\text{hr}}}\ \Big|\ \frac{5280\ \cancel{\text{ft}}}{1\ \cancel{\text{mi}}}\ \Big|\ \frac{12\ \cancel{\text{in}}}{1\ \cancel{\text{ft}}}\ \Big|\ \frac{2.54\ \text{cm}}{1\ \cancel{\text{in}}}\ \Big|\ \frac{1\ \cancel{\text{hr}}}{60\ \cancel{\text{min}}}\ \Big|\ \frac{1\ \cancel{\text{min}}}{60\ \text{sec}}$$

$$\text{rate} = \frac{(30)(5280)(12)(2.54)\ \text{cm}}{(60)(60)\ \ \text{sec}}$$

Q-11 A patient is to receive a certain medication at a dosage of 1.2 g per Kg of body weight. If the patient weighs 183 lb, how many grams of medication should he receive?

A-11 $$\frac{183\ \cancel{\text{lb}}}{}\ \Big|\ \frac{454\ \cancel{\text{g}}}{1\ \cancel{\text{lb}}}\ \Big|\ \frac{1\ \cancel{\text{Kg}}}{1000\ \cancel{\text{g}}}\ \Big|\ \frac{1.2\ \text{g medication}}{1\ \cancel{\text{Kg}}\ \text{body wt}}$$

$$\text{dosage} = \frac{(183)(454)(1.2)\ \text{g}}{(1000)}$$

Q-12 If the density of a certain substance is 3.2 lb per cubic ft (ft^3), what is the density in g per cm^3?

A-12 $$\frac{3.2\ \cancel{\text{lb}}}{1\ \cancel{\text{ft}^3}}\ \Big|\ \frac{454\ \text{g}}{1\ \cancel{\text{lb}}}\ \Big|\ \frac{1\ \cancel{\text{ft}^3}}{12^3\ \cancel{\text{in}^3}}\ \Big|\ \frac{1\ \cancel{\text{in}^3}}{(2.54)^3\ (\text{cm})^3}$$

$$\text{density} = \frac{(3.2)(454)\ \text{g}}{(12)^3(2.54)^3\ \text{cm}^3}$$

Q-13 The star nearest earth is 4.3 light years away (the distance light travels in one year). If light travels at the rate of $3 \cdot 10^{10}$ cm/sec, how many Angstroms away is this nearest star? (Hint: convert light years to light days to light hours, etc.)

A-13 $$\frac{4.3\ \cancel{\text{light years}}}{}\ \Big|\ \frac{365\ \cancel{\text{light days}}}{1\ \cancel{\text{light year}}}\ \Big|\ \frac{24\ \cancel{\text{light hours}}}{1\ \cancel{\text{light day}}}\ \Big|\ \frac{60\ \cancel{\text{light min}}}{1\ \cancel{\text{light hour}}}\ \Big|\ \frac{60\ \cancel{\text{light sec}}}{1\ \cancel{\text{light min}}}\ \Big|\ \frac{3 \cdot 10^{10}\ \cancel{\text{cm}}}{1\ \cancel{\text{light sec}}}\ \Big|\ \frac{10^8\ \text{Å}}{1\ \cancel{\text{cm}}}$$

$$\text{distance} = (4.3)(365)(24)(60)(60)(3)(10^{10})(10^8)\text{Å}$$

Q-14 A box 6" x 8" x 10" is completely filled with a liquid whose density is 1.27 g per cm^3. What will be the mass, <u>in pounds</u>, of the liquid filling the box?

A-14 $$\frac{6 \times 8 \times 10\ \cancel{\text{in}^3}}{}\ \Big|\ \frac{(2.54)^3\ \cancel{\text{cm}^3}}{1^3\ \cancel{\text{in}^3}}\ \Big|\ \frac{1.27\ \cancel{\text{g}}}{1\ \cancel{\text{cm}^3}}\ \Big|\ \frac{1\ \text{lb}}{454\ \cancel{\text{g}}}$$

$$\text{mass} = \frac{(6)(8)(10)(2.54)^3(1.27)\ \text{lb}}{454}$$

Q-15 A certain iron ore contains 5% iron. Assuming 100% recovery, how many tons of this ore would be required to produce 2.5 Kg of pure iron?

A-15 $$\frac{2.5\ \cancel{\text{Kg iron}}}{}\ \Big|\ \frac{1000\ \cancel{\text{g iron}}}{1\ \cancel{\text{Kg iron}}}\ \Big|\ \frac{1\ \cancel{\text{lb iron}}}{454\ \cancel{\text{g iron}}}\ \Big|\ \frac{100\ \cancel{\text{lb. ore}}}{5\ \cancel{\text{lb. iron}}}\ \Big|\ \frac{1\ \text{T ore}}{2000\ \cancel{\text{lb ore}}}$$

$$\text{tons of ore} = \frac{(2.5)(1000)(100)}{(454)(5)(2000)}$$

Q-16 A solution whose density was 0.890 g per cm^3 contained 2% (by weight) glucose. How many grams of glucose was contained in 17.2 liters of this solution?

(1 liter = 1000 cm^3)

A-16 $$\frac{17.2\ \cancel{\ell\ \text{solution}}}{}\ \Big|\ \frac{1000\ \cancel{\text{cm}^3\ \text{solution}}}{1\ \cancel{\ell\ \text{solution}}}\ \Big|\ \frac{0.890\ \cancel{\text{g solution}}}{1\ \cancel{\text{cm}^3\ \text{solution}}}\ \Big|\ \frac{2.0\ \text{g glucose}}{100\ \cancel{\text{g solution}}}$$

$$\text{g of glucose} = \frac{(17.2)(1000)(0.890)(2.0)}{100}$$

	LOGARITHMS										Proportional Parts								
No	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
No	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

	LOGARITHMS										Proportional Parts								
No	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
No	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

The proportional parts are stated in full for every tenth at the right-hand side The logarithm of any number of four significant figures can be read directly by adding the proportional part corresponding to the fourth figure to the tabular number corresponding to the first three figures There may be an error of 1 in the last place

NOTES

Chapter 2 | *STOICHIOMETRY*

Part I: Formulas, Atomic Weight, Molecular Weight, and Moles

After completing this section you should be able to

a) calculate the percentage composition, molecular weight, and the empirical and molecular formula of a compound
b) compute the number of moles in a given mass of an element or compound
c) calculate the approximate atomic weight of an element from its specific heat.

Part II: Equations

After completing this section you should be able to

a) balance oxidation-reduction equations
b) determine the relative number of moles and the relative masses of reactants and products in a reaction.

Part III: Concentrations of Solutions

After completing this section you should be able to

a) calculate the molarity of solutions
b) calculate the molality of solutions
c) calculate the percent solute in a solution
d) calculate the p[X] of a solution.

Part IV: Reactions in Solution

After completing this section you should be able to

a) calculate the volume of solutions needed for reactions
b) calculate the volume of gases produced in reactions.

Part V: Limiting Reagent and Percent Yield

After completing this section you should be able to

a) determine the limiting reagent in a reaction
b) calculate the percent yield of a reaction.

PART I: Formulas, Atomic Weight, Molecular Weight, and Moles

S-1 According to modern atomic theory, the chemical elements are composed of small, chemically discrete particles called atoms The atoms of different elements have different chemical properties Atoms of the same element or different elements may combine in certain simple ratios to form discrete particles called molecules Atoms may combine in more than one ratio to form more than one kind of molecule

Q-1 The molecule carbon dioxide, which has the formula CO_2, is composed of carbon and oxygen atoms. How many atoms of each element are present in each molecule of carbon dioxide?

A-1 Two atoms of oxygen and one atom of carbon.

Q-2 If two atoms of hydrogen and one atom of oxygen combine, what is the formula of the molecule formed?

A-2 H_2O

Q-3 Carbon and oxygen atoms may combine to form at least three different compounds where the carbon atom to oxygen atom ratios are 1:1, 1:2, and 3:2. What is the formula of the molecule in each of the compounds?

A-3 CO carbon monoxide
CO_2 carbon dioxide
C_3O_2 carbon suboxide

S-2 The weight of each element present in a sample of a compound may be determined by analytical procedures It is common to express this weight in terms of percent. This is known as percentage composition

$$\% \text{ composition} = \frac{\text{mass of element in sample}}{\text{total mass of sample}} \times 100$$

Q-4 A 0.500 gram sample of a compound was found to contain 0.200 grams of potassium (K). What is the percent of potassium in the sample?

A-4 $\frac{0.200 \text{ g of K}}{0.500 \text{ g of sample}} \times 100 = 40.0\%$

Q-5 A 1.237 gram sample of compound was found to contain 0.763 grams of palladium (Pd). What is the percent of palladium in the sample?

A-5 $\frac{0.763 \text{ g of Pd}}{1.237 \text{ g of sample}} \times 100 = 61.8\%$

Q-6 A 0.325 gram sample of some compound contained 15.0% calcium (Ca). What is the mass of calcium in the sample?

A-6 $\frac{0.325\ \cancel{\text{g sample}}}{} \Big| \frac{15.0\ \text{g Ca}}{100\ \cancel{\text{g sample}}}$

$= 0.0488$ g Ca

Q-7 A 1 346 gram sample of some compound contained 34 8% vanadium (V) What is the mass of vanadium in the sample?

A-7 $\frac{1.346\ \cancel{\text{g sample}}}{} \Big| \frac{34.8\ \text{g V}}{100\ \cancel{\text{g sample}}}$

$= 0.468$ g V

S-3 Every pure compound always contains definite, constant proportions or relative masses of the elements of which it is composed. This statement is known as the Law of Definite Composition.

Q-8 How will the percent of each element in a 10.0 gram sample of compound X compare with the percent of each element in a 30.0 gram sample of the same compound?

A-8 The percent of each element in the two samples of compound X will be the same.

Q-9 Why will the percent of each element in the two samples of compound X from Q-8 be the same?

A-9 The percentage composition in each molecule is the same. Increasing the number of molecules will not change the ratio of the atoms or percentage composition of the molecule.

Q-10 A sample of carbon dioxide contains 3.0 grams of carbon and 8.0 grams of oxygen How much oxygen will a sample of carbon dioxide contain which contains 10.0 grams of carbon?

A-10 $\frac{10\ \cancel{\text{g C}}}{} \Big| \frac{8.0\ \text{g O}}{3.0\ \cancel{\text{g C}}} = 27$ g oxygen

Q-11 A sample of sodium chloride (NaCl) contains 2.0 grams of Na and 3.0 grams of Cl. What percentage of the mass of the sodium chloride is sodium?

A-11 2.0 g Na
3.0 g Cl
5.0 g total

$\frac{2.0\ \text{g Na}}{5.0\ \text{g total}} \times 100 = 40\%$ Na

Q-12 A sample of lithium chloride (LiCl) contains 17% lithium by weight. If 10.0 grams of Li are allowed to react with an excess of chlorine to form LiCl, what mass of chlorine will combine with the 10.0 grams of Li?

A-12 100%
-17% Li
83% Cl

Consider 100 grams of compound: 17 grams of Li combine with 83 grams of Cl.

$\frac{10\ \cancel{\text{g Li}}}{} \Big| \frac{83\ \text{g Cl}}{17\ \cancel{\text{g Li}}} = 49$ g Cl

(amount which combines with 10.0 g Li)

S-4 Whenever two elements combine to produce more than one kind of compound, the relative masses of the one element which combine with a fixed mass of the second element may be expressed in a ratio of small whole numbers. This statement is known as the Law of Multiple Proportions

Q-13 Is the formula $C_{16}H_{18.5}$ consistent with the modern atomic theory? Why?

A-13 No. The molecules of a compound consist of combinations of whole atoms, never fractions of atoms

Q-14 If compound X has the molecular formula AB_3 and compound Y has the molecular formula A_2B_9, show that the ratio of B atoms in the two compounds which combine with like numbers of A atoms can be expressed in terms of small whole numbers.

A-14 Compound X
1 atom of A per 3 atoms of B
therefore
2 atoms of A per 6 atoms of B

Compound Y
2 atoms of A per 9 atoms of B

The ratio of atoms of B combining with two atoms of A in compounds X and Y is given as 6:9 or 2:3.

Q-15 The Law of Multiple Proportions is stated in terms of mass. Can we restate this law in terms of ratio of atoms? Why?

A-15 Yes. Since each atom has a definite mass, twice the number of atoms of a given element would have twice the mass. Therefore, the ratio of atoms and the ratio of total mass for a given element are identical.

Q-16 Elements A and B form two different compounds. In I, 0.50 grams of A are combined with 0.72 grams of B; in II, 0.15 grams of A are combined with 0.65 grams of B. Show that these data illustrate the Law of Multiple Proportions.

A-16 In compound I,

$$\frac{0.72\text{ g B}}{0.50\text{ g A}} = 1.4\frac{\text{g B}}{\text{g A}}$$ (amount of B which combines with 1 g A)

In compound II,

$$\frac{0.65\text{ g B}}{0.15\text{ g A}} = 4.3\frac{\text{g B}}{\text{g A}}$$ (amount of B which combines with 1 g A)

Therefore,

$$\frac{4.3\frac{\text{g B}}{\text{g A}}}{1.4\frac{\text{g B}}{\text{g A}}} = \frac{3}{1}$$

The mass of B which combines with 1 g A in two different compounds can be expressed in the ratio of small whole numbers.

Q-17 Ammonia contains 17.76% hydrogen and 82.24% nitrogen. When 3.77 grams of hydrogen react with 26.23 grams of nitrogen, 30.00 grams of hydrazine are formed. Show how these data for ammonia and hydrazine illustrate the Law of Multiple Proportions.

A-17 Consider 100 g ammonia

$$\frac{82.24\ g\ N}{17.76\ g\ H} = 4.63\ \frac{g\ N}{g\ H}$$

(amount of nitrogen which combines with 1 g of hydrogen in ammonia)

Consider hydrazine

$$\frac{26.23\ g\ N}{3.77\ g\ H} = 6.96\ \frac{g\ N}{g\ H}$$

(amount of nitrogen which combines with 1 g of hydrogen in hydrazine)

$$\frac{6.96\ \frac{g\ N}{g\ H}}{4.63\ \frac{g\ N}{g\ H}} = \frac{3}{2}$$

R If two elements combine to form more than one kind of compound, the relative mass of one element combined with a given mass of the other element may be expressed as a ratio of small whole numbers.

S-5 Atomic weight is defined as the mass of an atom of an element relative to a carbon atom. The carbon atom chosen as reference has arbitrarily been assigned an atomic weight of 12 00000 atomic mass units (amu).

Q-18 In terms of the arbitrary assignment of atomic weight, define one atomic mass unit

A-18 One atomic mass unit is 1/12 of the mass of a carbon atom.

Q-19 Carbon and oxygen atoms combine in the ratio of 1:1 in forming carbon monoxide, CO. It has been determined experimentally that 4.00 grams of oxygen combine with 3 00 grams of carbon in forming CO. According to these data, what is the ratio of the mass of one oxygen atom to one carbon atom? What is the atomic weight of oxygen in atomic mass units?

A-19 $$\frac{\text{mass of oxygen}}{\text{mass of carbon}} = \frac{4.00\ \cancel{g}}{3.00\ \cancel{g}} = \frac{4.00}{3.00}$$

$$\text{atomic weight oxygen} = \frac{4.00}{3.00}\ \text{(atomic weight carbon)}$$

$$= \frac{4.00}{3.00}\ (12.0\ \text{amu})$$

$$= 16.0\ \text{amu}$$

Q-20 Carbon and sulfur atoms combine in the ratio of 1:2 in forming carbon disulfide, CS_2. It has been determined experimentally that 16.0 grams of sulfur combine with 3.00 grams of carbon in forming CS_2. According to these data, what is the atomic weight of sulfur in atomic mass units?

A-20 $$\frac{\text{mass of sulfur}}{\text{mass of carbon}} = \frac{16.0\ \cancel{g}}{3.00\ \cancel{g}} = \frac{16.0}{3.00}$$

$$\text{mass of one sulfur atom} = \left(\frac{1}{2}\right)\left(\frac{16.0}{3.00}\right)\ \text{(mass of one carbon atom)}$$

$$\text{atomic weight of sulfur} = \frac{8.00}{3.00}\ (12.0\ \text{amu})$$

$$= 32.0\ \text{amu}$$

Q-21 A 2.00 gram sample of carbon combines with 0.670 gram of hydrogen in forming methane, CH_4 (four atoms of hydrogen to one atom of carbon). According to these data, what is the atomic weight of hydrogen in atomic mass units.

A-21 $\frac{\text{mass of hydrogen}}{\text{mass of carbon}} = \frac{0.670 \cancel{g}}{2.00 \cancel{g}} = 0.335$

mass of one hydrogen atom $= \frac{1}{4}$ (0.335) (mass of one carbon atom)

atomic weight of hydrogen $= \frac{1}{4}$ (0.335) (12.0 amu)

$= 1.00$ amu

Q-22 A 0.500 gram sample of nitrogen combines with 1.14 grams of oxygen in forming nitrogen dioxide, NO_2. According to these data, what is the atomic weight of nitrogen in atomic mass units.
(Hint: Once the atomic weight of an element has been found relative to that of carbon, it can be used as the reference in determining the atomic weight of an element which combines with it.)

A-22 $\frac{\text{mass of nitrogen}}{\text{mass of oxygen}} = \frac{0.500\ g}{1.14\ g} = 0.439$

atomic weight of nitrogen $= \frac{2}{1}$ (0.439) (16.0 amu)

$= 14.0$ amu

Q-23 The atomic weight of an element may be found in a periodic table (see cover). The values listed are in atomic mass units. What is the atomic weight of fluorine, F?

A-23 The atomic weight of fluorine is 19.0 (three significant figures).

Q-24 What is the atomic weight of sodium, Na?

A-24 The atomic weight of sodium is 23.0 (three significant figures).

[illegible]

S-6 A mole of atoms (referred to as a gram-atom) is defined as the collection of atoms whose total mass is the number of grams numerically equal to the atomic weight.

Q-25 What is the mass of one mole of silver ($_{47}Ag$)? (Consult the periodic table of elements.)

A-25 107.9 g

Q-26 What is the mass of one mole of sodium ($_{11}Na$)?

A-26 22.99 g

Q-27 How many moles are there in 75.4 g of sulfur ($_{16}S$)?

A-27 $\frac{75.4\ \cancel{g\ S}}{} \Big| \frac{1\ \text{mole S}}{32.1\ \cancel{g\ S}} = 2.35$ mole S

Q-28 By modern experimental techniques, the mass of one atom can be determined. If the mass of one sodium atom has been found to be 3.82×10^{-23} g, how many sodium atoms are contained in one mole of sodium?

A-28 $\dfrac{1 \text{ Na atom}}{3\ 82 \times 10^{-23} \cancel{\text{g Na}}} \left| \dfrac{22\ 99 \cancel{\text{g Na}}}{1 \text{ mole Na}} \right.$

$= 6\ 02 \times 10^{23} \dfrac{\text{atoms Na}}{\text{mole Na}}$

Q-29 If the mass of one oxygen atom has been found to be 2 66 x 10^{-23} g, how many oxygen atoms are contained in 1 mole of oxygen atoms?

A-29 $\dfrac{1 \text{ atom O}}{2.66 \times 10^{-23} \cancel{\text{g O}}} \left| \dfrac{16\ 00 \cancel{\text{g O}}}{1 \text{ mole O}} \right.$

$= 6\ 02 \times 10^{23} \dfrac{\text{atoms O}}{\text{mole O}}$

[redacted]

S-7 One mole of atoms (a gram-atom) of any element contains 6 02 x 10^{23} atoms of that element. This number is known as Avogadro's number.

Q-30 Knowing that one mole of carbon has a mass of 12.0 grams and contains Avogadro's number of atoms, calculate the mass of one atom of carbon?

A-30 $\dfrac{12\ 0 \text{ g C}}{1 \cancel{\text{mole C}}} \left| \dfrac{1 \cancel{\text{mole C}}}{6.02 \times 10^{23} \text{ atoms}} \right.$

$= 1\ 99 \times 10^{-23} \dfrac{\text{g C}}{\text{atom}}$

Q-31 How many atoms of potassium (K) are there in 30.7 grams of potassium?

A-31 $30.7 \cancel{\text{g K}} \left| \dfrac{1 \cancel{\text{mole K}}}{39.1 \cancel{\text{g K}}} \right| \dfrac{6.02 \times 10^{23} \text{ atoms K}}{1 \cancel{\text{mole K}}}$

$= 4\ 72 \times 10^{23}$ atoms of K

Q-32 How many atoms of strontium (Sr) are there in 10.0 grams of strontium?

A-32 $10.0 \cancel{\text{g Sr}} \left| \dfrac{1 \cancel{\text{mole Sr}}}{87.6 \cancel{\text{g Sr}}} \right| \dfrac{6.02 \times 10^{23} \text{atoms Sr}}{1 \cancel{\text{mole Sr}}}$

$= 6\ 87 \times 10^{22}$ atoms Sr

[redacted]

S-8 Just as atomic weight is defined as the mass of one atom relative to that of carbon-12, molecular weight is defined as the mass of one molecule relative to that of carbon-12. The molecular weight of a compound is calculated by adding together the atomic weights of all the atoms present in the molecule. This can be expressed mathematically as

$$\text{M.W.} = \sum_i n_i (\text{at. wt.})_i$$

where n_i is the number of i atoms, (at wt.)$_i$ is the atomic weight of the i^{th} atom, and the resultant product for each type of atom is summed up over all the atoms present in the molecule. (The molecular weight as defined above is sometimes referred to as formula weight.)

For example:

For CO_2 -- M.W. = (1)(12 0) + (2)(16.0)
= 44.0

For Fe_3O_4 -- M.W. = (3)(55.8) + (4)(16.0)
= 231.4

Q-33 What is the molecular weight of carbon tetrachloride (CCl_4)?

A-33 M.W. $= (1)(12.0) + (4)(35.5)$
$= 154.0$

Q-34 What is the molecular weight of sulfuric acid (H_2SO_4)?

A-34 M.W. $= (2)(1.01) + (1)(32.1) + 4(16.0)$
$= 98.1$

Q-35 What is the molecular weight of aluminum sulfate, $Al_2(SO_4)_3$?

A-35 M.W. $= (2)(27.0) + (3)(32.1) + (12)(16.0)$
$= 342.3$

Q-36 What is the molecular weight of $Mn(OH)_3$?

A-36 M.W. $= (1)(54.9) + (3)(16.0) + (3)(1.01)$
$= 105.9$

Q-37 What is the molecular weight of $Ga_2(CO_3)_3$?

A-37 M.W. $= (2)(69.7) + (3)(12.0) + (9)(16.0)$
$= 319.4$

R **M.W. $= \sum_i n_i\,(\text{at. wt.})_i$**

S-9 A mole of compound is defined as the collection of molecules whose total mass is the number of grams numerically equal to the molecular weight

Q-38 What is the mass of one mole of chlorine (Cl_2)?

A-38 molecular wt. $= 2(35.5)$
$= 71.0$ g

Q-39 What is the mass of three moles of aluminum bromide ($AlBr_3$)?

A-39 M.W $= 1(27.0) + 3(79.9) = 266.7$
$(266.7)(3) = 800.1$ g

Q-40 What is the mass of one molecule of carbon disulfide (CS_2)?

A-40 From the relationship of a mole of atoms to atomic weight and a mole of compound to molecular weight, one should be able to reason that in every mole of compound there is an Avogadro's number of molecules.

M.W. $= 12.0 + (2)(32.1) = 76.2$ g

$$\frac{76.2 \text{ g } CS_2}{1 \cancel{\text{ mole } CS_2}} \left| \frac{1 \cancel{\text{ mole } CS_2}}{6.02 \times 10^{23} \text{ molecule}} \right.$$

$$= 1.26 \times 10^{-22} \frac{\text{g } CS_2}{\text{molecule}}$$

Q-41 How many molecules of zinc sulfide (ZnS) are present in 50.1 grams of ZnS?

A-41 $$\frac{50.1 \cancel{\text{ g ZnS}}}{} \left| \frac{1 \cancel{\text{ mole ZnS}}}{97.5 \cancel{\text{ g ZnS}}} \right| \frac{6.02 \times 10^{23} \text{ molecules}}{1 \cancel{\text{ mole}}}$$

$= 3.09 \times 10^{23}$ molecules

Q-42 What is the percent of each element in manganese dioxide (MnO_2)?

A-42 Mass of 1 mole = 54.9 + (2)(16.0)

$= 86.9$ g

$\% \text{ Mn} = \dfrac{54.9 \text{ g Mn}}{86.9 \text{ g comp}} = 63.2\%$

$\% \text{ O} = \dfrac{32.0 \text{ g O}}{86.9 \text{ g comp}} = 36.8\%$

Q-43 What is the percent of each element in sodium thiosulfate ($Na_2S_2O_3$)?

A-43 Mass of 1 mole =

(2)(23.0) + (2)(32.1) + (3)(16.0)

= 158.2 g

$\% \text{ Na} = \dfrac{(2)(23.0) \text{g Na}}{158.2 \text{ g comp.}} \times 100 = 29.1\%$

$\% \text{ S} = \dfrac{(2)(32.1) \text{g S}}{158.2 \text{ g comp}} \times 100 = 40.6\%$

$\% \text{ O} = \dfrac{(3)(16.0) \text{g O}}{158.2 \text{ g comp}} \times 100 = 30.3\%$

Q-44 A molecule is made up of one atom of copper (Cu), two atoms of chromium (Cr), and seven atoms of oxygen (O). What is the percent of chromium in the molecule?

A-44 Mass of one mole =

(1)(63.5) + 2(52.0) + 7(16.0)

= 279.5 g

$\% \text{ Cr} = \dfrac{(2)(52.0) \text{g Cr}}{279 \text{ g comp.}} \times 100 = 37.2\%$

Q-45 In a specific compound, the percent of oxygen is 18.6%. There is one mole of <u>oxygen atoms</u> (a gram-atom) in each mole of the compound. What is the molecular weight of the compound?

A-45 100 grams of compound contains:

18.6 g oxygen
81.4 g other atoms

Thus: $\dfrac{81.4 \text{ g other atoms}}{18.6 \cancel{\text{g O}}} \left| \dfrac{16.0 \cancel{\text{g O}}}{1 \text{ mole comp}} \right.$

$= 70 \text{ g} \dfrac{\text{other atoms}}{\text{mole comp}}$

M.W. = 70 + 16 = 86

This problem can be done in one step:

$\dfrac{100 \text{ g comp}}{18.6 \cancel{\text{g O}}} \left| \dfrac{16 \cancel{\text{g O}}}{1 \text{ mole comp.}} \right. = 86 \text{ g/mole}$

M.W. = 86

Q-46 How many moles of hydrogen, phosphorus and oxygen are there in 0.213 moles of phosphoric acid (H_3PO_4)?

A-46 Hydrogen:

$\dfrac{0.213 \cancel{\text{mole } H_3PO_4}}{} \left| \dfrac{3 \text{ mole H}}{1 \cancel{\text{mole } H_3PO_4}} \right.$

= 0.639 mole H

Phosphorus:

$\dfrac{0.213 \cancel{\text{mole } H_3PO_4}}{} \left| \dfrac{1 \text{ mole P}}{1 \cancel{\text{mole } H_3PO_4}} \right.$

= 0.213 mole P

Oxygen:

$\dfrac{0.213 \cancel{\text{mole } H_3PO_4}}{} \left| \dfrac{4 \text{ mole O}}{1 \cancel{\text{mole } H_3PO_4}} \right.$

= 0.852 mole O

Q-47 How many moles of Ca and F would a sample of 2.01 moles of calcium fluoride (CaF_2) contain?

A-47 Calcium

$$\frac{2.01\ \cancel{\text{moles CaF}_2}}{} \bigg| \frac{1\ \text{mole Ca}}{1\ \cancel{\text{mole CaF}_2}} = 2.01\ \text{mole Ca}$$

Fluorine

$$\frac{2.01\ \cancel{\text{moles CaF}_2}}{} \bigg| \frac{2\ \text{mole F}}{1\ \cancel{\text{mole CaF}_2}} = 4.02\ \text{mole F}$$

Q-48 How many moles of barium carbonate, $Ba(CO_3)_2$, contain 1.06 moles of oxygen atoms?

A-48

$$\frac{1.06\ \cancel{\text{mole O}}}{} \bigg| \frac{1\ \text{mole Ba(CO}_3)_2}{6\ \cancel{\text{mole O}}} = 0.177\ \text{mole Ba(CO}_3)_2$$

Q-49 A sample of $Na_2B_4O_7$ contains 0.33 moles of oxygen atoms. How many moles of boron atoms does the sample contain?

A-49

$$\frac{0.33\ \cancel{\text{mole O}}}{} \bigg| \frac{1\ \cancel{\text{mole Na}_2\text{B}_4\text{O}_7}}{7\ \cancel{\text{mole O}}} \bigg| \frac{4\ \text{mole B}}{1\ \cancel{\text{mole Na}_2\text{B}_4\text{O}_7}} = 0.19\ \text{mole B}$$

Q-50 An impure sample of $Al_2(SO_4)_3$ weighs 2.732 grams. It was found to contain 7.75×10^{-3} moles of $Al_2(SO_4)_3$. What is the purity of the sample expressed in terms of % $Al_2(SO_4)_3$

A-50

$$\frac{7.75 \times 10^{-3}\ \cancel{\text{mole Al}_2(\text{SO}_4)_3}}{} \bigg| \frac{342\ \text{g Al}_2(\text{SO}_4)_3}{1\ \cancel{\text{mole Al}_2(\text{SO}_4)_3}} = 2.65\ \text{g Al}_2(\text{SO}_4)_3$$

$$\frac{2.65\ \text{g Al}_2(\text{SO}_4)_3}{2.73\ \text{g sample}} \times 100 = 97.1\%\ \text{Al}_2(\text{SO}_4)_3$$

Q-51 A sample of NaBr was found to contain 0.567 grams of Na. What mass of bromine (Br) should the sample contain?

A-51

$$\frac{0.567\ \cancel{\text{g Na}}}{} \bigg| \frac{1\ \cancel{\text{mole Na}}}{23.0\ \cancel{\text{g Na}}} \bigg| \frac{1\ \cancel{\text{mole Br}}}{1\ \cancel{\text{mole Na}}} \bigg| \frac{79.9\ \text{g Br}}{1\ \cancel{\text{mole Br}}} = 1.97\ \text{g Br}$$

Q-52 A sample of sodium chloride, NaCl, contaminated with KBr, weighs 0.225 grams. It was found to contain 0.0840 grams of sodium.

a) How many moles of Na did the sample contain?
b) How many moles of NaCl did the sample contain?
c) How many moles of Cl did the sample contain?
d) How many grams of NaCl did the sample contain?
e) What was the purity of the sample?

A-52

a) $$\frac{0.0840\ \cancel{\text{g Na}}}{} \bigg| \frac{1\ \text{mole Na}}{23.0\ \cancel{\text{g Na}}} = 3.65 \times 10^{-3}\ \text{mole Na}$$

b) $$\frac{3.65 \times 10^{-3}\ \cancel{\text{mole Na}}}{} \bigg| \frac{1\ \text{mole NaCl}}{1\ \cancel{\text{mole Na}}} = 3.65 \times 10^{-3}\ \text{mole NaCl}$$

c) $$\frac{3.65 \times 10^{-3}\ \cancel{\text{mole NaCl}}}{} \bigg| \frac{1\ \text{mole Cl}}{1\ \cancel{\text{mole NaCl}}} = 3.65 \times 10^{-3}\ \text{mole Cl}$$

d) $$\frac{3.65 \times 10^{-3}\ \cancel{\text{mole NaCl}}}{} \bigg| \frac{58.5\ \text{g NaCl}}{1\ \cancel{\text{mole NaCl}}} = 0.214\ \text{g NaCl}$$

e) $\dfrac{0.214 \text{ g NaCl} \times 100}{0.225 \text{ g total mass sample}} = 95.1\%$

Q-53 How many grams of hydrogen sulfide (H_2S) contain one half as many molecules of H_2S as there are atoms in 100 grams of iron (Fe)?

A-53 $\dfrac{100 \cancel{\text{ g Fe}}}{} \Big| \dfrac{1 \text{ mole Fe}}{55.8 \cancel{\text{ g Fe}}} = 1.79 \text{ mole Fe}$

$\dfrac{1.79 \cancel{\text{ mole}}}{} \Big| \dfrac{6.02 \times 10^{23} \text{ atoms}}{1 \cancel{\text{ mole}}}$

$= 1.08 \times 10^{24} \text{ atoms}$

$\dfrac{1.08 \times 10^{24} \cancel{\text{ atoms}}}{2} \Big| \dfrac{1 \cancel{\text{ mole } H_2S}}{6.02 \times 10^{23} \cancel{\text{ atoms}}} \Big| \dfrac{34.1 \text{ g}}{1 \cancel{\text{ mole } H_2S}} = 30.6 \text{ g } H_2S$

This problem can be done in one step

$\dfrac{100 \cancel{\text{ g Fe}}}{2} \Big| \dfrac{1 \cancel{\text{ mole Fe}}}{55.8 \cancel{\text{ g Fe}}} \Big| \dfrac{6.02 \times 10^{23} \cancel{\text{ atoms}}}{1 \cancel{\text{ mole}}} \Big| \dfrac{1 \cancel{\text{ mole } H_2S}}{6.02 \times 10^{23} \cancel{\text{ atoms}}} \Big| \dfrac{34.1 \text{ g } H_2S}{1 \cancel{\text{ mole } H_2S}} = 30.6 \text{ g } H_2S$

R
a) A mole of compound is the mass in grams numerically equal to the molecular weight.
b) One mole of a compound contains Avogadro's number of molecules (6.02×10^{23}).

S-10 The relative number of each kind of atom in a molecule may be calculated from the mass of the various atoms in the compound. The formula which gives the <u>simplest</u> ratio of the number of each kind of atom in a compound is called the <u>empirical</u> formula and may differ from the molecular formula. For example, benzene has a molecular formula of C_6H_6 and an empirical formula of CH.

Q-54 What is the molecular formula of a molecule if the empirical formula is NO_2 and the molecule contains two nitrogen atoms?

A-54 N_2O_4

Q-55 What is the empirical formula of a compound whose molecular formula is C_8H_{12}?

A-55 CH_2

Q-56 What is the empirical formula of a compound for which an analysis gave 0.326 mole of A and 0.655 mole of B?

A-56 $\dfrac{0.655 \text{ mole B}}{0.326 \text{ mole A}} = \dfrac{2 \text{ mole B}}{\text{mole A}}$

Therefore, there are twice the number of B atoms as A atoms in the molecule: AB_2

Q-57 What is the empirical formula of a compound for which an analysis gave 0.653 mole of K, 0.653 mole of Cl, and 1.306 mole of O?

A-57 $\dfrac{0.653 \text{ mole Cl}}{0.653 \text{ mole K}} = \dfrac{1 \text{ mole Cl}}{\text{mole K}}$

$\dfrac{1.306 \text{ mole O}}{0.653 \text{ mole K}} = \dfrac{2 \text{ mole O}}{\text{mole K}}$

Therefore, twice the number of O atoms as K and Cl: $KClO_2$

Q-58 The percentage composition of a compound was found to be 20.0% Ca and 80.0% Br. What is its empirical formula?

A-58 Consider 100 grams of compound

$$\frac{80.0\ \cancel{\text{g Br}}}{} \left| \frac{1\ \text{mole Br}}{79.9\ \cancel{\text{g Br}}} \right. = 1\ \text{mole Br}$$

$$\frac{20.0\ \cancel{\text{g Ca}}}{} \left| \frac{1\ \text{mole Ca}}{40.1\ \cancel{\text{g Ca}}} \right. = 0.5\ \text{mole Ca}$$

$$\frac{1\ \text{mole Br}}{0.5\ \text{mole Ca}} = \frac{2}{1}$$

Therefore, the empirical formula is $CaBr_2$

Q-59 The percentage composition of a compound was found to be 15.8% C and 84.2% S. What is its empirical formula?

A-59 Consider 100 grams of compound:

$$\frac{84.2\ \cancel{\text{g S}}}{} \left| \frac{1\ \text{mole S}}{32.1\ \cancel{\text{g S}}} \right. = 2.62\ \text{mole S}$$

$$\frac{15.8\ \cancel{\text{g C}}}{} \left| \frac{1\ \text{mole C}}{12.0\ \cancel{\text{g C}}} \right. = 1.32\ \text{mole C}$$

$$\frac{\text{mole S}}{\text{mole C}} = \frac{2.62}{1.32} = \frac{2}{1}$$

The empirical formula is CS_2

Q-60 The percentage composition of a compound was found to be 23.1% Al, 15.4% C, and 61.5% O. What is the empirical formula?

A-60 Consider 100 grams of compound:

$$\frac{23.1\ \cancel{\text{g Al}}}{} \left| \frac{1\ \text{mole Al}}{27.0\ \cancel{\text{g Al}}} \right. = 0.855\ \text{mole Al}$$

$$\frac{15.4\ \cancel{\text{g C}}}{} \left| \frac{1\ \text{mole C}}{12.0\ \cancel{\text{g C}}} \right. = 1.28\ \text{mole C}$$

$$\frac{61.5\ \cancel{\text{g O}}}{} \left| \frac{1\ \text{mole O}}{16.0\ \cancel{\text{g O}}} \right. = 3.84\ \text{mole O}$$

$$\frac{\text{mole C}}{\text{mole Al}} = \frac{1.28}{0.855} = 1.5\ \ (3\ \text{for}\ 2\ \text{Al})$$

$$\frac{\text{mole O}}{\text{mole Al}} = \frac{3.84}{0.855} = 4.5\ \ (9\ \text{for}\ 2\ \text{Al})$$

The empirical formula is $Al_2C_3O_9$.

Q-61 The percentage composition of a compound was found to be 65.8% Pb, 16.5% Cr, and 17.7% O. What is the empirical formula of the compound?

A-61 Consider 100 grams of compound:

$$\frac{65.8\ \cancel{\text{g Pb}}}{} \left| \frac{1\ \text{mole Pb}}{207.2\ \cancel{\text{g Pb}}} \right. = 0.318\ \text{mole Pb}$$

$$\frac{16.5\ \cancel{\text{g Cr}}}{} \left| \frac{1\ \text{mole Cr}}{52.0\ \cancel{\text{g Cr}}} \right. = 0.317\ \text{mole Cr}$$

$$\frac{17.7\ \cancel{\text{g O}}}{} \left| \frac{1\ \text{mole O}}{16.0\ \cancel{\text{g O}}} \right. = 1.11\ \text{mole O}$$

$$\frac{0.317\ \text{mole Cr}}{0.318\ \text{mole Pb}} = 1\ \ (2\ \text{Cr for}\ 2\ \text{Pb})$$

$$\frac{1.11\ \text{mole O}}{0.318\ \text{mole Pb}} = 3.5\ (7\ \text{O for}\ 2\ \text{Pb})$$

The empirical formula is $Pb_2Cr_2O_7$.

Q-62 The empirical formula of a compound is CH_2. The molecular weight is 84. What is the molecular formula of the compound?

A-62 Empirical weight of CH_2 =

$$12 + (2)(1) = 14$$

$$\frac{84 \text{ M.W}}{14 \text{ E.W}} = 6$$

Molecular formula. $(CH_2)_6 = C_6H_{12}$

Q-63 A compound has an empirical formula of HgCl If its molecular weight is 472, what is its molecular formula?

Ch

A-63 Empirical weight of HgCl =

$$200.6 + 35.5 = 236.1$$

$$\frac{472 \text{ M.W.}}{236 \text{ E.W.}} = 2$$

Molecular formula: $(HgCl)_2 = Hg_2Cl_2$

Q-64 A compound was found to contain 1.20 grams of sulfur (S) and 1.30 grams of chromium (Cr) What is the empirical formula of this compound? If the molecular weight of the compound is 600, what is the molecular formula?

A-64 $\dfrac{1.20 \cancel{\text{g S}}}{} \Big| \dfrac{1 \text{ mole S}}{32.1 \cancel{\text{g S}}} = 0.0374 \text{ mole S}$

$\dfrac{1.30 \cancel{\text{g Cr}}}{} \Big| \dfrac{1 \text{ mole Cr}}{52.0 \cancel{\text{g Cr}}} = 0.0250 \text{ mole Cr}$

$$\frac{0.0374 \text{ mole S}}{0.0250 \text{ mole Cr}} = 1.5 = \frac{3}{2}$$

empirical formula: Cr_2S_3
empirical weight: 200

$$\frac{600 \text{ M.W.}}{200 \text{ E.W.}} = 3$$

Molecular formula: $(Cr_2S_3)_3 = Cr_6S_9$

Q-65 In a binary compound, a compound which contains only two kinds of atoms, the number of atoms of hydrogen is 2.25 times the number of carbon atoms. One-tenth of a mole of the compound weighs 11.4 grams. What is the molecular formula?

A-65 $(11.4)(10) = 114$ g = molecular weight

empirical formula = $CH_{2.25}$ = C_4H_9
empirical weight = 57 g

$$\frac{114 \text{ g M.W.}}{57.0 \text{ g E.W.}} = 2$$

Molecular formula: $(C_4H_9)_2 = C_8H_{18}$

Q-66 The percent of nitrogen in a compound is 20.0% and there are 2.00 moles of nitrogen atoms per mole of compound. What is the molecular weight of the compound?

A-66 100 g of compound contains 20.0 g of nitrogen. Therefore,

$$\frac{100 \text{ g compound}}{20.0 \cancel{\text{g N}}} \Big| \frac{14.0 \cancel{\text{g N}}}{1 \cancel{\text{mole N atoms}}} \Big| \frac{2 \cancel{\text{mole N atoms}}}{1 \text{ mole compound}} = \frac{(100)(14.0)(2)}{(20.0)} \frac{\text{g compound}}{\text{mole compound}} = 140 \text{ g/mole}$$

Q-67 When the binary compound X is decomposed completely, the mass of carbon is always approximately 6 times the mass of hydrogen. 0.250 mole of X weighs 21.0 grams. What is the molecular formula?

A-67 Mass of 1 mole of X = (4)(21 0) = 84 g
Out of every 7 parts, 6 parts are carbon and 1 part is hydrogen

$$\frac{84\ 0}{7} = 12\ 0 \text{ g H}$$

$$12\ 0 \times 6 = 72\ 0 \text{ g C}$$

$$\frac{12\,\cancel{\text{g H}}}{} \left|\, \frac{1 \text{ mole H}}{1\,\cancel{\text{g H}}} \right. = 12 \text{ mole H}$$

$$\frac{72\,\cancel{\text{g C}}}{} \left|\, \frac{1 \text{ mole C}}{12\,\cancel{\text{g C}}} \right. = 6 \text{ mole C}$$

molecular formula. C_6H_{12}

R a) The empirical formula is the relative number of each kind of atom in a molecule.
b) The molecular formula is the total number of each kind of atom in a molecule.

S-11 The Law of Dulong and Petit states that the atomic weight of a solid element is approximately equal to 6.3 calories per mole per degree divided by the specific heat of the element in calories per gram per degree Thus, if the specific heat of an element is

$$0.274 \frac{\text{cal}}{\text{g-deg}},$$

the approximate atomic weight = $\frac{6.3\,\cancel{\text{cal}}}{\text{mole-}\cancel{\text{degree}}} \left|\, \frac{\text{g-}\cancel{\text{degree}}}{0.274\,\cancel{\text{cal}}} \right. = 23$ g mole

Q-68 Determine the approximate atomic weight of an element, X, if it has a specific heat of 0.053 calories per gram-degree.

A-68 Atomic weight =

$$\frac{6.3\,\cancel{\text{cal}}}{\text{mole-}\cancel{\text{degree}}} \left|\, \frac{\text{g-}\cancel{\text{degree}}}{0.053\,\cancel{\text{cal}}} \right. = 119 \text{ g/mole}$$

Q-69 The element chromium (Cr), has a specific heat of 0.122 calories per gram-degree. If 3.121 grams of chromium combines with oxygen to form 4.561 grams of oxide, what is the approximate and exact atomic weight of chromium (1 mole of O atoms 16.00 g)

A-69 Approximate atomic weight of Cr·

$$\frac{6\ 3\,\cancel{\text{cal}}}{\text{mole-}\cancel{\text{degree}}} \left|\, \frac{\text{g-}\cancel{\text{degree}}}{0.122\,\cancel{\text{cal}}} \right. = 51.6 \text{ g/mole}$$

mass of oxygen atoms in sample of oxide
= 4.561 g oxide - 3.121 g Cr
= 1.440 g O in oxide

Q-70 When 13.2151 grams of lead (Pb) were heated in an excess of air, the resulting lead oxide was found to weigh 15.2560 grams. If the specific heat of lead is 0.031 calories per gram-degree, calculate the approximate atomic weight and the exact atomic weight of lead.

$$\frac{1.440\,\cancel{\text{g O}}\text{ in oxide}}{} \left|\, \frac{1 \text{ mole O atoms}}{16.00\,\cancel{\text{g O}}} \right. = 0.090 \text{ mole O atoms in oxide sample}$$

$$\frac{3.121\,\cancel{\text{g Cr}}\text{ in oxide}}{} \left|\, \frac{1 \text{ mole Cr atoms}}{\text{approx. } 51.6\,\cancel{\text{g Cr}}} \right. = 0.0605 \text{ mole Cr atoms in oxide sample}$$

$$\frac{0.090 \text{ mole O atoms}}{0.060 \text{ mole Cr atoms}} = 1.5 = \frac{3}{2}$$

empirical formula = Cr_2O_3

The exact atomic weight of Cr is

$$\frac{3.121 \text{ g Cr}}{1.44\,\cancel{\text{g O}}} \left|\, \frac{16\ 0\,\cancel{\text{g O}}\text{ atoms}}{1\,\cancel{\text{mole O}}\text{ atoms}} \right|\, \frac{3\,\cancel{\text{mole O}}\text{ atoms}}{2 \text{ mole Cr atoms}} = 52.0 \frac{\text{g Cr}}{\text{mole Cr atoms}}$$

A-70 Approximate atomic weight of Pb·

$$\frac{6.3 \cancel{\text{cal}}}{\text{mole-}\cancel{\text{degree}}} \left| \frac{\text{g-}\cancel{\text{degree}}}{0.031 \cancel{\text{cal}}} \right. = 204 \text{ g} \frac{\text{Pb}}{\text{mole}}$$

mass of O atoms in sample = 15.2560 - 13.2151 = 2.0409 g

$$\frac{2.0409 \cancel{\text{g O}}}{} \left| \frac{1 \text{ mole O atoms}}{16.0 \cancel{\text{g O}}} \right. = 0.127 \text{ mole O atoms}$$

$$\frac{13.2151 \cancel{\text{g Pb}}}{} \left| \frac{1 \text{ mole Pb atoms}}{\text{approx. } 204 \cancel{\text{g Pb}}} \right. = 0.0648 \text{ mole Pb atoms}$$

$$\frac{0.127 \text{ mole O atoms}}{0.0648 \text{ mole Pb atoms}} = 1.96 \approx 2$$

empirical formula = PbO_2

Exact atomic weight·

$$\frac{13.2151 \text{ g Pb}}{2.0409 \cancel{\text{g O}}} \left| \frac{16.00 \cancel{\text{g O}}}{1 \cancel{\text{mole O atoms}}} \right| \frac{2 \cancel{\text{mole O atoms}}}{1 \text{ mole Pb atoms}} = \frac{207.8 \text{ g Pb}}{\text{mole Pb atoms}}$$

R Atomic weight $\approx \dfrac{6.3}{\text{specific heat}}$

PART II: Equations

S-1 A chemical equation represents a chemical reaction. The reactants are written on the left side and the products on the right side of the equation.

Q-1 Consider the following chemical equation

$$A + B \rightarrow C + D$$

What are the reactants and products in this reaction?

A-1 **reactants: A and B**
products: C and D

Q-2 Given the following equation·

$$2H_2 + O_2 \rightarrow 2H_2O$$

What are the reactants and products?

A-2 **reactants: H_2 and O_2**
products: H_2O

Q-3 Given the following equation:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

What are the reactants and products?

A-3 **reactants: Fe, H_2O**
products: Fe_3O_4, H_2

S-2 The chemical equation, $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$, specifies that 3 moles of Fe atoms will react with 4 moles of H_2O molecules to give 1 mole of Fe_3O_4 and 4 moles of H_2 molecules.

Q-4 According to the following reaction, how many moles of water will be formed when 2 moles of H_2 and one mole of O_2 react?

$$2H_2 + O_2 \rightarrow 2H_2O$$

A-4 According to the equation, 2 moles of H_2 react with one mole of O_2 to give 2 moles of H_2O

Q-5 According to the following reaction how many moles of water are produced when a mole of H_2SO_4 reacts with 2 moles of NaOH?

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

A-5 1 mole of sulfuric acid reacts with 2 moles of sodium hydroxide to yield 1 mole of sodium sulfate (Na_2SO_4) and 2 moles of water.

Q-6 If one mole of silver nitrate ($AgNO_3$) reacted with ½ mole of hydrogen sulfide (H_2S) according to the following equation, how many moles of silver sulfide (Ag_2S) would be formed?

$$H_2S + 2AgNO_3 \rightarrow Ag_2S + 2HNO_3$$

A-6 1 mole of H_2S reacts with 2 moles of $AgNO_3$ to give 1 mole of Ag_2S. Therefore, ½ mole of H_2S will react with 1 mole of $AgNO_3$ to give ½ mole Ag_2S.

Q-7 In the following equation, how many moles of oxygen atoms are indicated on the reactants side of the equation?

$$FeCl_3 + 3AgNO_3 \rightarrow 3AgCl + Fe(NO_3)_3$$

A-7 1 mole of ferric chloride ($FeCl_3$) and 3 moles of silver nitrate react. Each mole of $AgNO_3$ contains 3 moles of O atoms. Therefore, there are 3 x 3 or 9 moles of O atoms indicated on the reactant side of the equation

Q-8 In the equation given in the previous question, how many moles of oxygen atoms are indicated on the products side of the equation?

A-8 3 moles of AgCl and 1 mole of $Fe(NO_3)_3$ were produced. Each mole of $Fe(NO_3)_3$ contains 9 moles of O atoms. Therefore, 9 moles of O atoms are indicated on the product side of the equation.

Q-9 Are the same number of moles of oxygen atoms indicated on both the reactant and product side of the equation given in Q-7? Are the same number of moles of silver atoms indicated on both sides of the equation?

A-9 Yes, the equation given in Q-7 indicates 9 moles of oxygen atoms on both the reactant and product side of the equation. Three moles of silver atoms are indicated on both sides of the equation.

S-3 A chemical equation must be balanced. When an equation is balanced, it is consistent with the conservation of mass and conservation of electrical charge. In a balanced equation the number of atoms and electrical charges on the left hand side must equal those on the right hand side of the equation.

Q-10* Is the following equation balanced?

$$NaI + AgNO_3 \rightarrow AgI + NaNO_3$$

A-10 Yes Conservation of mass is satisfied

Q-11 Equations are balanced by placing coefficients in front of the chemical formulas in such a way that the same number of moles of each atom is indicated on both sides of the equation The ratio of atoms in a chemical formula is never altered (i e , in balancing an equation, H_2O may be changed to $2H_2O$, but never to H_4O_2 or HO)

Balance the following equation

$$NaOH + H_2S \rightarrow Na_2S + H_2O$$

A-11 Inspection shows that there are two Na atoms on the right and one on the left, so the coefficient, 2, is placed in front of NaOH. Then another coefficient, 2, is placed in front of H_2O to balance H and O. The general rule is to balance H and O last

$$2NaOH + H_2S \rightarrow Na_2S + 2H_2O$$

Q-12 Balance the following equation

$$Ca(OH)_2 + HCl \rightarrow CaCl_2 + H_2O$$

A-12 $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

Q-13 Balance the following equation

$$NaF + Ca(NO_3)_2 \rightarrow CaF_2 + NaNO_3$$

A-13 $2NaF + Ca(NO_3)_2 \rightarrow CaF_2 + 2NaNO_3$

Q-14 Balance the following equation

$$NaI + Pb(NO_3)_2 \rightarrow PbI_2 + NaNO_3$$

A-14 $2NaI + Pb(NO_3)_2 \rightarrow PbI_2 + 2NaNO_3$

R A balanced chemical equation gives
a) reactants and products in a chemical reaction
b) relationship between moles and masses of reactants and products in a chemical reaction

S-4 Before proceeding to balance more complicated equations, the concept of oxidation numbers of the elements must be understood. Oxidation numbers are assigned according to arbitrary rules. Free elements are assigned an oxidation number of zero Oxygen in compounds is assigned an oxidation number of -2. Hydrogen in compounds is assigned an oxidation number of +1. The sum of the oxidation numbers for a neutral molecule must equal zero. The sum of the oxidation numbers for an ionic species is equal to the charge on the ion.

Q-15 Assign oxidation numbers to the elements in the following species.

a) H_2

b) H_2O

c) P_4

d) Al

A-15

	oxidation number
a) H_2	H is zero
b) H_2O	H is +1 O is -2
c) P_4	P is zero
d) Al	Al is zero

Q-16 An exception to the rule given above for oxygen occurs in compounds called peroxides These compounds have oxygen-oxygen bonds In these cases oxygen is assigned an oxidation number of -1

Assign oxidation numbers to oxygen in the following compounds

a) H_2SO_4
b) H_2O_2 hydrogen peroxide
c) HNO_3
d) BaO_2 barium peroxide

A-16 oxidation number of oxygen

a) -2
b) -1 (peroxide)
c) -2
d) -1 (peroxide)

Q-17 An exception to the rule given for hydrogen occurs in compounds called hydrides. In hydrides, hydrogen is assigned an oxidation number of -1.

Assign oxidation numbers to hydrogen in the following compounds

a) HCl
b) H_2O_2
c) NaH sodium hydride
d) HNO_3
e) CaH_2 calcium hydride

A-17 oxidation number of hydrogen

a) +1
b) +1
c) -1
d) +1
e) -1

Q-18 Assign oxidation numbers to all the elements in the following compounds.

a) LiH lithium hydride
b) Na_2O sodium oxide
c) Na_2O_2 sodium peroxide
d) KH potassium hydride

A-18

a) Li H
+1 -1

b) Na O
+1 -2

c) Na O
+1 -1

d) K H
+1 -1

Q-19 Li, Na, and K all belong to Group I in the periodic table. What general rule could be given for assigning oxidation numbers to the Group I (alkali) elements in compounds?

A-19 All Group I elements are assigned an oxidation number of +1.

Q-20 Assign oxidation numbers to all elements in the following compounds.

a) CaH_2 calcium hydride
b) BaO_2 barium peroxide
c) SrO strontium oxide

A-20

a) Ca H
+2 -1

b) Ba O
+2 -1

c) Sr O
+2 -2

Q-21 Ca, Ba and Sr all belong to Group II in the periodic table. What general rule could be given for assigning oxidation numbers to the Group II (alkaline-earth) elements in compounds.

A-21 All Group II elements are assigned an oxidation number of +2.

Q-22 Remember that for an ionic species the oxidation numbers are assigned so that the sum of the oxidation numbers equal the charge on the ion. For example in ClO_4^-, if oxygen is assigned an oxidation number of -2, then chlorine must be assigned an oxidation number of +7. The sum of oxidation numbers is

$+7 + 4(-2) = -1$ = charge on the ion

Assign oxidation numbers for the elements in the following species.

a) NO_3^-

b) OH^-

c) Na^+

A-22

a) N +5, O -2

b) O -2, H +1

c) Na +1

Q-23 Assign oxidation numbers for the elements in the following species.

a) SO_4^{-2}

b) NO_2^-

c) Al^{+3}

A-23

a) S +6, O -2

b) N +3, O -2

c) Al +3

Q-24 Assign oxidation numbers to all the elements in the following species.

a) MnO_4^-

b) $Fe(OH)_3$

c) $Na_2S_2O_3$

d) CO_3^{-2}

e) NaCl

f) BeF_2

A-24

a) Mn +7, O_4 -2

b) Fe +3, O -2, H +1

c) Na +1, S +2, O -2

d) C +4, O -2

e) Na +1, Cl -1

f) Be +2, F -1

Q-25 In the following reaction does the oxidation number of sulfur change in going from reactants to products?

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

A-25 No.

H_2SO_4: S +6

Na_2SO_4: S +6

Q-26 In the following reaction does the oxidation number of hydrogen or oxygen change in going from reactants to products?

$$H^+ + OH^- \rightarrow H_2O$$

A-26 No.

H^+: +1

OH^-: -2 +1

H_2O: +1 -2

Q-27 In the following reaction does the oxidation number of nitrogen change in going from reactants to products?

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$$

A-27 No

HNO_3 $Ca(NO_3)_2$
+5   +5

H. Oxidation numbers are assigned as follows:

a) free element = [illegible]
b) oxygen in a compound = -2 (-1 for per[illegible])
c) hydrogen in a compound = +1 (-1 for [illegible])
d) group I metals in a compound = +1
e) group II metals in a compound = +2
f) sum of the oxidation numbers of a neutral molecule = 0
g) sum of the oxidation numbers of an ion = charge on the ion

S-5 Oxidation-reduction reactions involve a change of oxidation number An element is oxidized if its oxidation number increases (becomes more positive) in going from reactant to product. An element is reduced if its oxidation number is decreased in going from reactant to product

Q-28 Consider the following reaction·

$$2H_2 + O_2 - 2H_2O$$

Assign oxidation numbers to all the elements in both reactants and products.

A-28 $2H_2 + O_2 \rightarrow 2H_2O$
0   0   +1 -2

Q-29 How does the oxidation number of hydrogen change in this reaction? Does it increase or decrease?

A-29 Hydrogen goes from zero to +1, an increase in oxidation number

Q-30 If an element's oxidation number is increased, is it oxidized or reduced?

A-30 Oxidized

Q-31 How does the oxidation number of oxygen change in the reaction, $2H_2 + O_2 - 2H_2O$? Is oxygen oxidized or reduced?

A-31 Oxidation number decreases. Oxygen is reduced

Q-32 Assign oxidation numbers to all the elements in the following reaction and determine which elements are oxidized and which are reduced.

$$2Na + 2H_2O - 2NaOH + H_2$$

A-32 $2Na + 2H_2O \rightarrow 2NaOH + H_2$
0   +1 -2   +1-2+1   0

Na   0 to +1   oxidized
H   +1 to 0   reduced

Q-33 Assign oxidation numbers to all the elements in the following equation and determine which are oxidized and which are reduced.

$$2Al + 2NaOH + 2H_2O - 2NaAlO_2 + 3H_2$$

A-33 $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
0   +1-2+1   +1 -2   +1 +3 -2   0

Al   0 to +3   oxidized
H   +1 to 0   reduced

Q-34 Assign oxidation numbers to all the elements in the following reaction and determine which are oxidized and which are reduced.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

(Hint: Na_2O_2 is called sodium peroxide)

A-34 $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$
$\quad +1\ -1 \quad +1\ -2 \quad +1\ -2\ +1 \quad 0$

Oxygen is both oxidized and reduced It goes from -1 to zero and from -1 to -2 This is called auto-oxidation-reduction

R Oxidation - increase in oxidation number
Reduction - decrease in oxidation number

S-6 Assignment of the change in oxidation number is the first step in the balancing of a complicated oxidation-reduction reaction The second step is to determine the magnitude of the change in oxidation number per atom and then per molecule

Q-35 Determine the change in oxidation number per atom and per molecule in the following reaction (unbalanced).

$$Fe_2O_3 + H_2 \rightarrow Fe + H_2O$$

A-35 $Fe_2O_3 + H_2 \rightarrow Fe + H_2O$
$\quad +3\ -2 \quad 0 \quad 0 \quad +1\ -2$

Each iron atom undergoes a change of oxidation number of three The change per molecule of Fe_2O_3 is

$$2(3) = 6$$

Each hydrogen atom undergoes a change of oxidation number of one. The change per molecule of hydrogen (H_2) is

$$2(1) = 2$$

Q-36 Determine the magnitude of the change in oxidation number per atom and per molecule in the following reaction (unbalanced)

$$Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$$

A-36 The sulfate radical (SO_4) has a net charge of -2. Therefore, sulfur is assigned an oxidation number of +6.

$Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$
$\quad 0 \quad +1+6-2 \quad +3\ +6-2 \quad 0$

Each Al atom has a change of oxidation number of 3. Each H atom has a change of oxidation number of one Therefore, the change per molecule of H_2SO_4 is

$$2(1) = 2 .$$

Q-37 Determine the change of oxidation number per atom and molecule in the following reaction (unbalanced)

$$C_6H_6 + O_2 \rightarrow CO_2 + H_2O$$
(benzene)

A-37 $C_6H_6 + O_2 \rightarrow CO_2 + H_2O$
$\quad -1\ +1 \quad 0 \quad +4\ -2 \quad +1\ -2$

Each carbon atom undergoes a change of oxidation number of 5 (from -1 to +4). The change per molecule of benzene, C_6H_6, is

$$6(5) = 30 .$$

Each oxygen atom undergoes a change of oxidation number of 2. The change per molecule of oxygen is

$$2(2) = 4 .$$

S-7 The third step in balancing oxidation-reduction reactions is to make the total gain in oxidation number equal the total decrease in oxidation number This is done by placing the proper coefficients in front of the molecules with atoms that undergo a change in oxidation number. The final step is to balance the rest of the equation by inspection.

Q-38 In the equation, $Fe_2O_3 + H_2 \rightarrow Fe + H_2O$, the oxidation number change per molecule of Fe_2O_3 was -6 and the oxidation number change per molecule of H_2 was +2 How many molecules of H_2 must undergo a change to equal the oxidation number change of Fe_2O_3?

A-38 Each molecule of Fe_2O_3 undergoes a change of 6 To balance this change, 3 molecules of H_2 must undergo a change, i. e

6 (change in Fe_2O_3) = 3 x 2 (change in H_2)

Q-39 Write the equation showing that 3 moles of H_2 react with one mole of Fe_2O_3.

A-39 $Fe_2O_3 + \underline{3}H_2 \rightarrow Fe + H_2O$

Q-40 Note that in the equation given in the last answer, the number of moles of Fe atoms, H atoms, and O atoms are not the same on each side of the equation. Balance the Fe atoms by inserting the proper coefficients into the right hand side of the equation. Then balance the hydrogen and oxygen atoms by the same process.

A-40 $Fe_2O_3 + 3H_2 \rightarrow Fe + H_2O$

Step 1: $Fe_2O_3 + 3H_2 \rightarrow 2Fe + H_2O$
Step 2: $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$

Q-41 Balance the following equation.

$Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$

A-41 Assign oxidation numbers and the change in oxidation numbers. Each Al changes from 0 to +3 Since there are two Al atoms in the product, $Al_2(SO_4)_3$, the overall increase must be

$$2(3) = 6$$

Each H changes from +1 to 0. Since there are two H atoms per molecule of H_2SO_4, the overall change per molecule of H_2SO_4 is

$$2(1) = 2 .$$

Thus, to make the oxidation number-increase equal the oxidation number-decrease, three H_2SO_4 molecules must undergo change for every two Al atoms undergoing change. To balance the equation a 2 is placed in front of Al and a 3 in front of H_2SO_4. The equation is finally balanced by placing a 3 in front of H_2.

$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$

Q-42 Balance the following equation.

$H_3AsO_4 + H_2S \rightarrow H_3AsO_3 + S + H_2O$

A-42 The equation is balanced as written

As $+5 \rightarrow +3$ change of 2

S $-2 \rightarrow 0$ change of 2

Q-43 Balance the following equation

$(NH_4)_2Cr_2O_7 \rightarrow N_2 + H_2O + Cr_2O_3$

Note The (NH_4) radical has a +1 charge.

A-43 $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$

N $-3 \rightarrow 0$ change of 3 (change of 6 per mole of $(NH_4)_2Cr_2O_7$)

Cr $+6 \rightarrow +3$ change of 3 (change of 6 per mole of $(NH_4)_2Cr_2O_7$)

Q-44 Balance the following equation.

$KMnO_4 + FeCl_2 + HCl \rightarrow$
$KCl + H_2O + MnCl_2 + FeCl_3$

A-44 $KMnO_4 + 5FeCl_2 + 8HCl \rightarrow$
$MnCl_2 + 5FeCl_3 + 4H_2O + KCl$

Mn $+7 \rightarrow +2$ change of 5

Fe $+2 \rightarrow +3$ change of 1

Q-45 Balance the following equation.

$Sn + HNO_3 + H_2O \rightarrow H_{10}Sn_5O_{15} + NO$

A-45 $15Sn + 20HNO_3 + 5H_2O \rightarrow 3H_{10}Sn_5O_{15}$
$+ 20NO$

Sn $0 \rightarrow +4$ change of 4 (change of 20 per molecule $H_{10}Sn_5O_{15}$)

N $+5 \rightarrow +2$ change of 3

Q-46 Balance the following equation.

$MnO_2 + HCl \rightarrow Cl_2 + MnCl_2 + H_2O$

(Hint: Some of the chlorine atoms do not change oxidation number in this reaction.)

A-46 $MnO_2 + 4HCl \rightarrow Cl_2 + MnCl_2 + 2H_2O$

Mn $+4 \rightarrow +2$ change of 2

Cl $-1 \rightarrow 0$ change of 1 (change of 2 for each molecule of Cl_2 formed)

In order to balance the chlorine which is not oxidized ($MnCl_2$), a 4 must be placed in front of the HCl.

Q-47 Balance the following equation.

$Zn + HNO_3 \rightarrow Zn(NO_3)_2 + N_2O + 5H_2O$

A-47 $4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

Zn $0 \rightarrow +2$ change of 2

N $+5 \rightarrow +1$ change of 4

Q-48 Balance the following equation.

$Mn(NO_3)_2 + NaBiO_3 + HNO_3 \rightarrow$
$NaMnO_4 + Bi(NO_3)_3 + NaNO_3 + H_2O$

A-48 $2Mn(NO_3)_2 + 5NaBiO_3 + 14HNO_3 \rightarrow$
$2NaMnO_4 + 5Bi(NO_3)_3 + 3NaNO_3 + 7H_2O$

Mn $+2 \rightarrow +7$ change of 5

Bi $+5 \rightarrow +3$ change of 2

S-8 Since a balanced equation gives the relative number of moles of reactants and products, the quantity of all the reactants and products can be determined provided the quantity of one of the reactants or products is known This can be done by constructing unity factors Consider the following equation

$$2H_2 + O_2 \rightarrow 2H_2O$$

Because 2 moles of H_2 react with one mole of O_2 to yield 2 moles of H_2O, the following unity factors are appropriate

$$\frac{2 \text{ mole } H_2}{1 \text{ mole } O_2} \qquad \frac{2 \text{ mole } H_2}{2 \text{ mole } H_2O} \qquad \frac{1 \text{ mole } O_2}{2 \text{ mole } H_2O}$$

Q-49 Use the unit conversion method to show how many moles of O_2 would be needed to react completely with 0 50 moles of H_2 according to the equation

$$2H_2 + O_2 \rightarrow 2H_2O$$

A-49 $0.50 \cancel{\text{mole } H_2} \times \frac{1 \text{ mole } O_2}{2 \cancel{\text{mole } H_2}} = 0\ 25 \text{ mole } O_2$

Q-50 How many moles of H_2O would be produced by 0.80 moles of O_2, according to the equation

$$2H_2 + O_2 \rightarrow 2H_2O$$

A-50 $0\ 80 \cancel{\text{mole } O_2} \times \frac{2 \text{ mole } H_2O}{1 \cancel{\text{mole } O_2}} = 1.6 \text{ mole } H_2O$

Q-51 Given the following equation

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

How many moles of O_2 would be needed to react completely with 0.300 moles of C_2H_6 (ethane).

A-51 $0.300 \cancel{\text{mole } C_2H_6} \times \frac{7 \text{ mole } O_2}{2 \cancel{\text{mole } C_2H_6}}$

$= 1.05 \text{ mole } O_2$

Q-52 According to the equation in Q-51, how many moles of CO_2 would be produced by 3 moles of C_2H_6?

A-52 $3 \cancel{\text{mole } C_2H_6} \times \frac{4 \text{ mole } CO_2}{2 \cancel{\text{mole } C_2H_6}}$

$= 6 \text{ mole } CO_2$ produced

Q-53 According to the balanced equation

$$3C_3H_6 + 4H_2O + 2KMnO_4 \rightarrow 3C_3H_8O_2 + 2MnO_2 + 2KOH$$

determine the following:

a) the number of moles of $KMnO_4$ needed to react with 0.900 moles of C_3H_6.
b) the number of moles of MnO_2 produced by 0.600 moles of C_3H_6.

A-53 a) $0.900 \cancel{\text{mole } C_3H_6} \times \frac{2 \text{ mole } KMnO_4}{3 \cancel{\text{mole } C_3H_6}}$

$= 0.600 \text{ mole } KMnO_4$

b) $0.600 \cancel{\text{mole } C_3H_6} \times \frac{2 \text{ mole } MnO_2}{3 \cancel{\text{mole } C_3H_6}}$

$= 0.400 \text{ mole } MnO_2$

Q-54 Since a mole of an element or compound represents a certain mass of the element or compound, the balanced equation gives the relative masses of reactants and products. According to the balanced equation

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

how many grams of Fe will react with 4.00 moles of H_2O?

A-54 $\dfrac{4.00\ \cancel{\text{mole } H_2O}}{} \Big| \dfrac{3\ \cancel{\text{mole Fe}}}{4\ \cancel{\text{mole } H_2O}} \Big| \dfrac{55.8\text{ g Fe}}{1\ \cancel{\text{mole Fe}}} = 167\text{ g Fe}$

Q-55 How many grams of iron would be needed to produce 23.1 grams of Fe_3O_4 according to the equation given in Q-54?

A-55 $\dfrac{23.1\ \cancel{\text{g } Fe_3O_4}}{} \Big| \dfrac{1\ \cancel{\text{mole } Fe_3O_4}}{231\ \cancel{\text{g } Fe_3O_4}} \Big| \dfrac{3\ \cancel{\text{mole Fe}}}{1\ \cancel{\text{mole } Fe_3O_4}} \Big| \dfrac{55.8\text{ g Fe}}{1\ \cancel{\text{mole Fe}}} = 16.7\text{ g Fe}$

Q-56 How many grams of Fe_3O_4 would be produced by 36.0 g of water according to the reaction given in Q-54?

A-56 $\dfrac{36.0\ \cancel{\text{g } H_2O}}{} \Big| \dfrac{1\ \cancel{\text{mole } H_2O}}{18.0\ \cancel{\text{g } H_2O}} \Big| \dfrac{1\ \cancel{\text{mole } Fe_3O_4}}{4\ \cancel{\text{mole } H_2O}} \Big| \dfrac{231\text{ g } Fe_3O_4}{1\ \cancel{\text{mole } Fe_3O_4}} = 115\text{ g } Fe_3O_4$

Q-57 Given the following equation:

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$$

Calculate the grams of Fe_2O_3 needed to produce 20.0 g of Fe.

A-57 $\dfrac{20.0\ \cancel{\text{g Fe}}}{} \Big| \dfrac{1\ \cancel{\text{mole Fe}}}{55.8\ \cancel{\text{g Fe}}} \Big| \dfrac{1\ \cancel{\text{mole } Fe_2O_3}}{2\ \cancel{\text{mole Fe}}} \Big| \dfrac{160\text{ g } Fe_2O_3}{1\ \cancel{\text{mole } Fe_2O_3}} = 28.7\text{ g } Fe_2O_3$

Q-58 Calculate the grams of Al_2O_3 produced by 5.00 g of Al metal reacted according to the equation given in Q-57.

A-58 $\dfrac{5.00\ \cancel{\text{g Al}}}{} \Big| \dfrac{1\ \cancel{\text{mole Al}}}{27.0\ \cancel{\text{g Al}}} \Big| \dfrac{1\ \cancel{\text{mole } Al_2O_3}}{2\ \cancel{\text{mole Al}}} \Big| \dfrac{102\text{ g } Al_2O_3}{1\ \cancel{\text{mole } Al_2O_3}} = 9.44\text{ g } Al_2O_3$

PART III: Concentrations of Solutions

S-1 If a chemical reaction is carried out in solution, the quantities of chemicals involved are expressed in units of concentration. Two terms commonly used in expressing concentration are:

solute - the substance that is dissolved
solvent - the substance in which the solute is dissolved

Molarity is defined as the number of moles of solute per liter of solution.

Q-1 If 58.5 g of NaCl is dissolved in enough water to make one liter of solution, calculate the molarity of the resulting solution.

A-1

$$\frac{58.5\ \cancel{\text{g NaCl}}}{1\ \text{liter solution}}\ \Bigg|\ \frac{1\ \text{mole NaCl}}{58.5\ \cancel{\text{g NaCl}}}$$

$$= \frac{1\ \text{mole NaCl}}{1\ \text{liter solution}}$$

(This would be called a one molar solution, abbreviated 1 M.)

Q-2 If 20.0 g of NaCl is dissolved in enough water to make 500 ml of solution, calculate the molarity of the solution.

A-2

$$\frac{20.0\ \cancel{\text{g NaCl}}}{500\ \cancel{\text{ml solution}}}\ \Bigg|\ \frac{1\ \text{mole NaCl}}{58.5\ \cancel{\text{g NaCl}}}\ \Bigg|\ \frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter solution}}$$

$$= 0.684\ \frac{\text{mole NaCl}}{1\ \text{liter solution}}$$

$$= 0.684\,M$$

Q-3 If 40 g of $CuSO_4$ is dissolved in enough water to make 250 ml of solution, calculate the molarity of the solution.

A-3

$$\frac{40\ \cancel{\text{g } CuSO_4}}{250\ \cancel{\text{ml solution}}}\ \Bigg|\ \frac{1\ \text{mole } CuSO_4}{160\ \cancel{\text{g } CuSO_4}}\ \Bigg|\ \frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter solution}}$$

$$= 1.0\ \frac{\text{mole } CuSO_4}{\text{liter solution}}$$

$$= 1.0\ M$$

Q-4 What mass of $AlCl_3$ would be needed to make 100 ml of 0.100 molar $AlCl_3$ solution?

A-4

$$100\ \cancel{\text{ml solution}}\ \Bigg|\ \frac{1\ \cancel{\text{liter solution}}}{1000\ \cancel{\text{ml solution}}}\ \Bigg|\ \frac{0.100\ \cancel{\text{mole } AlCl_3}}{1\ \cancel{\text{liter solution}}}\ \Bigg|\ \frac{133\ \text{g } AlCl_3}{1\ \cancel{\text{mole } AlCl_3}} = 13.3\ \text{g } AlCl_3$$

Q-5 What mass of $AgNO_3$ would be needed to make 250 ml of 0.500 molar $AgNO_3$ solution?

A-5

$$250\ \cancel{\text{ml solution}}\ \Bigg|\ \frac{1\ \cancel{\text{liter solution}}}{1000\ \cancel{\text{ml solution}}}\ \Bigg|\ \frac{0.500\ \cancel{\text{mole } AgNO_3}}{1\ \cancel{\text{liter solution}}}\ \Bigg|\ \frac{170\ \text{g } AgNO_3}{1\ \cancel{\text{mole } AgNO_3}} = 21.2\ \text{g } AgNO_3$$

Q-6 Another concentration that is commonly used is molality.

molality = the number of moles of solute per kilogram (kg) of solvent.

If 120 g of $MgSO_4$ is dissolved in 1000 g of water, calculate the molality of the solution.

A-6

$$\frac{120\ \cancel{\text{g } MgSO_4}}{1000\ \cancel{\text{g solvent}}}\ \Bigg|\ \frac{1\ \text{mole } MgSO_4}{120\ \cancel{\text{g } MgSO_4}}\ \Bigg|\ \frac{1000\ \cancel{\text{g solvent}}}{1\ \text{kg solvent}} = \frac{1\ \text{mole } MgSO_4}{\text{kg solvent}}$$

This is called a 1 molal solution, 1 m.

Q-7 Why isn't the 1 molal solution given in the preceding question equivalent to a 1 molar solution?

A-7 A 1 molar solution would contain 1 mole of solute per liter of solution, while a 1 molal solution would contain 1 mole of solute per kilogram of solvent.

Q-8 Calculate the molality of a solution made by dissolving 50 g of $CaCO_3$ in 1000 g of H_2O.

A-8 $\dfrac{50\ \cancel{g\ CaCO_3}}{1000\ \cancel{g\ solvent}} \cdot \dfrac{1\ mole\ CaCO_3}{100\ \cancel{g\ CaCO_3}} \cdot \dfrac{1000\ \cancel{g\ solvent}}{1\ kg\ solvent}$

$= \dfrac{0.50\ mole\ CaCO_3}{1\ kg\ solvent}$

$= 0.50\ m$

Q-9 Calculate the molality of a solution made by dissolving 20.0 g of KCl in 250 g of H_2O

A-9 $\dfrac{20.0\ \cancel{g\ KCl}}{250\ \cancel{g\ solvent}} \cdot \dfrac{1\ mole\ KCl}{74.5\ \cancel{g\ KCl}} \cdot \dfrac{1000\ \cancel{g\ solvent}}{1\ kg\ solvent}$

$= 1.07\ \dfrac{mole\ KCl}{kg\ solvent}$

$= 1.07\ m$

Q-10 Calculate the number of grams of CaF_2 that must be added to 250 g of H_2O to make a 2.00 molal CaF_2 solution.

A-10 $250\ \cancel{g\ solvent} \cdot \dfrac{1\ \cancel{kg\ solvent}}{1000\ \cancel{g\ solvent}} \cdot \dfrac{2.00\ \cancel{mole\ CaF_2}}{1\ \cancel{kg\ solvent}} \cdot \dfrac{78.0\ g\ CaF_2}{1\ \cancel{mole\ CaF_2}} = 39.0\ g\ CaF_2$

Q-11 Calculate the number of grams of $BaCl_2$ that must be added to 100 g of H_2O to make a 0.100 molal $BaCl_2$ solution

A-11 $100\ \cancel{g\ solvent} \cdot \dfrac{1\ \cancel{kg\ solvent}}{1000\ \cancel{g\ solvent}} \cdot \dfrac{0.100\ \cancel{mole\ BaCl_2}}{1\ \cancel{kg\ solvent}} \cdot \dfrac{208\ g\ BaCl_2}{1\ \cancel{mole\ BaCl_2}} = 2.08\ g\ BaCl_2$

S-2 Concentration is sometimes expressed in percent of solute, that is, the percent by mass that the solute contributes to the total mass of the solution. If a solution is said to be 3% NaCl, it contains 3.0 g of NaCl per 100 g of solution.

Q-12 How many grams of $CaCl_2$ would be needed to make 200 g of 5.0% $CaCl_2$ solution?

A-12 $200\ \cancel{g\ solution} \cdot \dfrac{5.0\ g\ CaCl_2}{100\ \cancel{g\ solution}}$

$= 10\ g\ CaCl_2$

Q-13 How many grams of $BaCO_3$ would be needed to make 10 g of 0.20% $BaCO_3$ solution?

A-13 $10\ \cancel{g\ solution} \cdot \dfrac{0.20\ g\ BaCO_3}{100\ \cancel{g\ solution}}$

$= 0.02\ g\ BaCO_3$

Q-14 What is the percent of solute in a solution which contains 40.0 g of solute per 250 g of solution?

A-14 $\dfrac{40.0\ g\ solute}{250\ \cancel{g\ solution}} \cdot 100\ \cancel{g\ solution}$

= 16.0 g in 100 g solution

= 16.0%

Q-15 What is the percent of solute in a solution which contains 10.0 g LiBr in 2500 g of solution?

A-15

$$\frac{10.0 \text{ g solute}}{2500 \cancel{\text{ g solution}}} \left| \frac{100 \cancel{\text{ g solution}}}{} \right.$$

$= 0.400$ g in 100 g solution

$= 0.400\%$

Q-16 The density of a solution is expressed as mass per unit volume of solution. The most common unit for liquids is grams per milliliter

The density of a KOH solution was determined and found to be 1.25 g per ml.

Calculate the mass of 1.00 liter of the KOH solution

A-16

$$\frac{1.25 \text{ g solution}}{1 \cancel{\text{ ml solution}}} \left| \frac{1000 \cancel{\text{ ml solution}}}{1 \text{ liter of solution}} \right.$$

$= 1.25 \times 10^3 \frac{\text{g}}{\text{liter of solution}}$

Q-17 If a CaF_2 solution has a density of 1.30 g/ml, calculate the mass of 250 ml of this solution.

A-17

$$\frac{1.30 \text{ g solution}}{1 \cancel{\text{ ml solution}}} \left| \frac{250 \cancel{\text{ ml solution}}}{} \right.$$

$= 325$ g solution

Q-18 If the density and the percent of solute in a solution are known, the molarity and molality may be calculated. The following questions illustrate the method.

A $MgCl_2$ solution has a density of 1.119 g per ml and the percent of solute is 29.0%.

Calculate the mass of 1.00 liter of solution.

A-18

$$\frac{1.119 \text{ g solution}}{1 \cancel{\text{ ml solution}}} \left| \frac{1000 \cancel{\text{ ml solution}}}{1 \text{ liter of solution}} \right.$$

$= 1.119 \times 10^3 \frac{\text{g}}{\text{liter of solution}}$

Q-19 Calculate the mass of $MgCl_2$ in one liter of the solution in Q-18.

(Hint: Remember that % is defined as mass of solute per 100 g of solution.)

A-19

$$\frac{1.119 \times 10^3 \cancel{\text{ g solution}}}{1 \text{ liter solution}} \left| \frac{29.0 \text{ g } MgCl_2}{100 \cancel{\text{ g solution}}} \right.$$

$= 325 \frac{\text{g } MgCl_2}{\text{liter solution}}$

Q-20 **Remembering that the solution described in Q-18 contains 325 grams of $MgCl_2$ per liter of solution and has a mass of 1.12×10^3 grams per liter of solution, calculate the molarity of the solution in Q-18.**

A-20

$$\frac{325 \cancel{\text{ g } MgCl_2}}{1 \text{ liter solution}} \left| \frac{1 \text{ mole } MgCl_2}{95.3 \cancel{\text{ g } MgCl_2}} \right.$$

$= 3.41 \frac{\text{mole } MgCl_2}{\text{liter solution}}$

$= 3.41$ M

Q-21 **Calculate the molality of the solution in Q-18.**

Hint: Calculate the mass of water per liter of solution. (mass of 1 liter solution) - (mass of $MgCl_2$ per liter solution) = mass of water per liter of solution.

A-21 1119 g - 325 g = 794 g water per liter solution

$$\frac{3.41 \text{ mole}}{1 \cancel{\text{ liter solution}}} \left| \frac{1 \cancel{\text{ liter solution}}}{794 \cancel{\text{ g water}}} \right| \frac{1000 \cancel{\text{ g water}}}{1 \text{ kg water}}$$

$= 4.29 \frac{\text{moles}}{\text{kg water}}$

$= 4.29$ m

Q-22 **A barium chloride ($BaCl_2$) solution has a density of 1.279 grams per milliliter and the percent of solute is 26.0%.**

Calculate the molarity of this solution.

A-22
$$\frac{1.279\ \cancel{\text{g solution}}}{1\ \cancel{\text{ml solution}}}\Big|\frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter solution}}\Big|\frac{26.0\ \cancel{\text{g BaCl}_2}}{100\ \cancel{\text{g solution}}}\Big|\frac{1\ \text{mole BaCl}_2}{208\ \cancel{\text{g BaCl}_2}}$$

$$1.60\ \frac{\text{mole BaCl}_2}{\text{liter solution}}$$

$= 1.60$ M

Q-23 Calculate the molality of the solution in Q-22

A-23
$$\frac{1.279\ \cancel{\text{g solution}}}{1\ \cancel{\text{ml solution}}}\Big|\frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter solution}}\Big|\frac{26.0\ \text{g BaCl}_2}{100\ \cancel{\text{g solution}}} = 332\ \frac{\text{g BaCl}_2}{\text{liter solution}}$$

1279 g solution - 332 g $BaCl_2$ = 947 g water per liter of solution

$$\frac{1.60\ \text{mole BaCl}_2}{1\ \cancel{\text{liter solution}}}\Big|\frac{1\ \cancel{\text{liter solution}}}{947\ \cancel{\text{g water}}}\Big|\frac{1000\ \cancel{\text{g water}}}{1\ \text{kg water}}$$

$$= 1.69\ \frac{\text{mole BaCl}_2}{1\ \text{kg water}}$$

$= 1.69$ m

Q-24 An ammonium sulfate, $(NH_4)_2SO_4$, solution has a density of 1.289 g per ml and a percent of solute of 50.0%.

Calculate the molarity of this solution.

A-24
$$\frac{1.289\ \cancel{\text{g solution}}}{1\ \cancel{\text{ml solution}}}\Big|\frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter of solution}}\Big|\frac{50.0\ \cancel{\text{g (NH}_4)_2\text{SO}_4}}{100\ \cancel{\text{g solution}}}\Big|\frac{1\ \text{mole (NH}_4)_2\text{SO}_4}{132\ \cancel{\text{g (NH}_4)_2\text{SO}_4}}$$

$$4.88\ \frac{\text{mole (NH}_4)_2\text{SO}_4}{\text{liter solution}}$$

$= 4.88$ M

Q-25 Calculate the molality of the solution in Q-24.

A-25
$$\frac{1.289\ \cancel{\text{g solution}}}{1\ \cancel{\text{ml solution}}}\Big|\frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter solution}}\Big|\frac{50.0\ \text{g (NH}_4)_2\text{SO}_4}{100\ \cancel{\text{g solution}}} = 644\ \frac{\text{g (NH}_4)_2\text{SO}_4}{\text{liter solution}}$$

1289 g solution - 644 g $(NH_4)_2SO_4$ = 645 g water per liter of solution

$$\frac{4.88\ \text{mole (NH}_4)_2\text{SO}_4}{1\ \cancel{\text{liter solution}}}\Big|\frac{1\ \cancel{\text{liter solution}}}{645\ \cancel{\text{g water}}}\Big|\frac{1000\ \cancel{\text{g water}}}{1\ \text{kg water}}$$

$$= 7.57\ \frac{\text{mole (NH}_4)_2\text{SO}_4}{1\ \text{kg water}}$$

$= 7.57$ m

Q-26 A solution of chromium sulfate, $Cr_2(SO_4)_3$, has a density of 1.489 grams per ml and is 40.0% in solute.

Calculate the molarity of $Cr_2(SO_4)_3$ in this solution.

A-26
$$\frac{1.489\ \cancel{\text{g solution}}}{1\ \cancel{\text{ml solution}}}\Big|\frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter solution}}\Big|\frac{40.0\ \cancel{\text{g Cr}_2(\text{SO}_4)_3}}{100\ \cancel{\text{g solution}}}\Big|\frac{1\ \text{mole Cr}_2(\text{SO}_4)_3}{392\ \cancel{\text{g Cr}_2(\text{SO}_4)_3}}$$

$$= 1.52\ \frac{\text{mole Cr}_2(\text{SO}_4)_3}{\text{liter solution}}$$

$= 1.52$ M

Q-27 Calculate the molality of the solution in Q-26.

A-27
$$\frac{1.489\ \cancel{\text{g solution}}}{1\ \cancel{\text{ml solution}}}\Big|\frac{1000\ \cancel{\text{ml solution}}}{1\ \text{liter solution}}\Big|\frac{40.0\ \text{g Cr}_2(\text{SO}_4)_3}{100\ \cancel{\text{g solution}}} = 596\ \frac{\text{g Cr}_2(\text{SO}_4)_3}{\text{liter solution}}$$

1489 g solution - 596 g $Cr_2(SO_4)_3$ = 893 g water per liter of solution

$$\frac{1.52\ \text{mole Cr}_2(\text{SO}_4)_3}{1\ \cancel{\text{liter solution}}}\Big|\frac{1\ \cancel{\text{liter solution}}}{893\ \cancel{\text{g water}}}\Big|\frac{1000\ \cancel{\text{g water}}}{1\ \text{kg water}}$$

$$= 1.70\ \frac{\text{mole Cr}_2(\text{SO}_4)_3}{1\ \text{kg water}}$$

$= 1.70$ m

S-3 Chemists frequently use brackets ([ ]) to denote moles/liter or molar concentration.

$[X^-]$ = concentration of ion X^- in moles/liter.

It is often convenient to denote molar concentrations of ions as negative logs of concentrations The symbol "p" is used to denote -log

Thus, $-\log[X^-] = p[X^-]$ If $[X^-] = 2.3 \times 10^{-4}$ then,

$$\begin{aligned} p[X^-] &= -\log[X^-] \\ &= -\log(2.3 \times 10^{-4}) \\ &= -(\log 2.3 + \log 10^{-4}) \\ &= 3.64 \end{aligned}$$

Q-28 If $[H^+] = 5.67 \times 10^{-4}$, what is $p[H^+]$?

A-28 $$\begin{aligned} p[H^+] &= -\log(5.67 \times 10^{-4}) \\ &= -(0\ 7536 - 4) \\ &= -(-3\ 2464) \\ &= 3.25 \end{aligned}$$

Q-29 If $[Cl^-] = 3.89 \times 10^{-3}$, what is $p[Cl^-]$?

A-29 $$\begin{aligned} p[Cl^-] &= -\log(3.89 \times 10^{-3}) \\ &= -(0.5899 - 3) \\ &= -(-2.4101) \\ &= 2.41 \end{aligned}$$

Q-30 If $[OH^-] = 8.23 \times 10^{-7}$, what is $p[OH^-]$?

A-30 $$\begin{aligned} p[OH^-] &= -\log(8.23 \times 10^{-7}) \\ &= -(0.9154 - 7) \\ &= 6.08 \end{aligned}$$

S-4 Ions in solution do not act as independent particles. They "feel" the attractions and repulsions of other ions in the same solution. Because of these attractive and repulsive forces, the "effective concentration" of ions is less than the number of particles actually present. We call this effective concentration the activity; activity is equal to the concentration of particles times a correction factor called the activity coefficient. The activity coefficient varies with the concentration of ions, becoming smaller as concentration becomes larger. the pH of a solution (not to be confused with $p[H^+]$) is defined as

$-\log$ [activity of hydrogen ion] $= -\log[a_{H^+}]$, or

$-\log$ [activity coefficient x hydrogen ion concentration]

In dilute solutions, the activity coefficient is very nearly one. Thus, for a solution in which the $[H^+]$ (concentration of H^+ ion in moles/liter) is 3.62×10^{-5}, the activity coefficient is close to one, and the pH can be approximated as

$$\begin{aligned} pH &= -\log(3.62 \times 10^{-5}) \\ &= -(\log 3.62 + \log 10^{-5}) \\ &= -(0.5587) + (-5) \\ &= 4.44 \end{aligned}$$

Q-31 Assuming an activity coefficient of one, what is the pH of a solution with $[H^+] = 4\ 91 \times 10^{-9}$?

A-31
$$\begin{aligned} pH &= -\log([H^+] \times \text{activity coefficient}) \\ &-\log(4\ 91 \times 10^{-9} \times 1) \\ &= -(\log 4.91 + \log 10^{-9}) \\ &-[(0.6911) + (-9)] \\ &= 8.31 \end{aligned}$$

Q-32 Assuming an activity coefficient of one, what is the pH of a solution with $[H^+] = 3\ 83 \times 10^{-13}$?

A-32
$$\begin{aligned} pH &= -\log(3.83 \times 10^{-13} \times 1) \\ &-(\log 3.83 + \log 10^{-13}) \\ &-[(0.5832) + (-13)] \\ &12.42 \end{aligned}$$

Q-33 Assuming an activity coefficient of 0.997, what is the pH of a solution with $[H^+] = 4.50 \times 10^{-3}$?

A-33
$$\begin{aligned} pH \quad &-\log[(4.50 \times 10^{-3})(9.97 \times 10^{-1})] \\ &-[(0.6532) + (-3) + (0.9987) + (-1)] \\ &2\ 35 \end{aligned}$$

S-5 **To find the hydrogen ion activity from pH,** rewrite pH as a whole number and a <u>negative</u> **decimal. For example, if pH = 5.21, write it as 6 +** (-0.79).

$$\begin{aligned} \text{Since } pH = -\log[a_{H^+}] &= 6 + (-0.79) \\ \log[a_{H^+}] &= -6 + 0.79 \\ [a_{H^+}] &= 10^{-6} \times 10^{0.79} \\ \text{antilog } 0.79 &= 6.17 \\ [a_{H^+}] &= 10^{-6} \times 6.17 \end{aligned}$$

Q-34 Find the $[a_{H^+}]$ of a solution whose pH = 2.71.

A-34
$$\begin{aligned} pH = 2.71 &= 3.00 + (-0.29) \\ -\log[a_{H^+}] &= 3.00 + (-0.29) \\ \log[a_{H^+}] &= -3.00 + 0.29 \\ [a_{H^+}] &= 10^{-3} \times 10^{0.29} \\ &= 1.95 \times 10^{-3} \end{aligned}$$

Q-35 If the pH of a solution is 9.87, what is $[a_{H^+}]$?

A-35
$$\begin{aligned} -\log[a_{H^+}] &= 9.87 = 10.00 + (-0.13) \\ \log[a_{H^+}] &= -10 + 0.13 \\ \cancel{[a_{H^+}]} &\cancel{= 10^{-10} \times 10^{0.13}} \\ &= 1.35 \times 10^{-10} \end{aligned}$$

Q-36 Find $[a_{H^+}]$ of a solution whose pH = 7.13.

A-36 $pH = 7.13 = 8.0 + (-0.87)$

$-\log[a_{H^+}] = 8\ 0 + (-0.87)$

$\log[a_{H^+}] = -8\ 0 + 0.87$

$[a_{H^+}] = 10^{-8} \times 10^{0\ 87}$

$= 7.41 \times 10^{-8}$

Q-37 Find $[a_{H^+}]$ of a solution whose pH = 8.88

A-37 $pH = 9.0 + (-0\ 12)$

$-\log[a_{H^+}] = 9\ 0 + (-0\ 12)$

$\log[a_{H^+}] = -9\ 0 + 0\ 12$

$[a_{H^+}] = 10^{-9} \times 10^{0.12}$

$= 1.32 \times 10^{-9}$

Q-38 Find the pH of a solution whose $[a_{H^+}] = 3\ 81 \times 10^{-5}$.

A-38 $pH = -\log[a_{H^+}]$

$= -\log 3\ 81 \times 10^{-5}$

$= -(\log 3.81 + \log 10^{-5})$

$= -(0\ 581 + -5)$

$= 4.42$

Q-39 Find the pH of a solution whose $[H^+] = 3\ 22 \times 10^{-2}$ and activity coefficient = 0.98.

A-39 $pH = -\log[a_{H^+}] = -\log[H^+](a.c.)$

$= -\log[(3.22 \times 10^{-2})(9\ 8 \times 10^{-1})]$

$= -[0.508 + (-2) + 0.991 + (-1)]$

$= 1.50$

[illegible]

PART IV: Reactions in Solution

S-1 When a reaction is carried out in solution, it is possible to calculate the volume of solution necessary for complete reaction if the concentrations of the reactants in solution are known. Any of the concentration units discussed in the preceding problems may be used.

Q-1 If an aqueous solution of $CuNO_3$ and $Hg(NO_3)_2$ reacts according to the following equation

$$2Hg(NO_3)_2 + 2CuNO_3 \rightarrow Hg_2(NO_3)_2 + 2Cu(NO_3)_2,$$

how many moles of $Hg(NO_3)_2$ would be needed to react completely with 30.0 ml of 0.100 molar $CuNO_3$?

A-1 $\dfrac{30.0\ \cancel{ml}}{} \left| \dfrac{0.100\ \cancel{mole}}{1000\ \cancel{ml}} \right| \dfrac{2\ mole\ Hg(NO_3)_2}{2\ \cancel{mole}\ Cu(NO_3)}$

$= 0.00300$ mole

$= 3.00 \times 10^{-3}$ mole

Q-2 What volume of 0.100 molar $Hg(NO_3)_2$ would be needed to provide the moles of $Hg(NO_3)_2$ calculated in A-1?

A-2 $\dfrac{3.00 \times 10^{-3}\ \cancel{mole}}{} \left| \dfrac{1000\ ml}{0.100\ \cancel{mole}} \right.$

$= 30.0$ ml

Q-3 Given the following reaction:

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

Calculate the volume of 0 250 molar $SnCl_2$ needed to react completely with 35.0 ml of 0.200 molar $FeCl_3$.

A-3 $\dfrac{35.0\ \cancel{ml\ FeCl_3}\ solution}{} \left| \dfrac{0.200\ \cancel{mole\ FeCl_3}}{1000\ \cancel{ml\ FeCl_3}} \right| \dfrac{1\ \cancel{mole\ SnCl_2}}{2\ \cancel{mole\ FeCl_3}} \left| \dfrac{1000\ ml\ SnCl_2\ solution}{0.250\ \cancel{mole\ SnCl_2}} \right.$

$= 14.0$ ml $SnCl_2$ solution

Q-4 Given the following equation:

$$Hg_2Cl_{2(s)} + SnCl_2 \rightarrow SnCl_4 + 2Hg$$

Calculate the volume of 0.100 molar stannous chloride, $SnCl_2$, needed to react completely with 50.0 g of solid Hg_2Cl_2.

A-4 $\dfrac{50.0\ \cancel{g\ Hg_2Cl_2}}{} \left| \dfrac{1\ \cancel{mole\ Hg_2Cl_2}}{472\ \cancel{g\ Hg_2Cl_2}} \right| \dfrac{1\ \cancel{mole\ SnCl_2}}{1\ \cancel{mole\ Hg_2Cl_2}} \left| \dfrac{1\ liter\ SnCl_2\ solution}{0.1\ \cancel{mole\ SnCl_2}} \right. = 1.06$ liters $SnCl_2$ solution

Q-5 Given the following equation:

$$SnCl_4 + Fe_{(s)} \rightleftharpoons FeCl_2 + SnCl_2$$

Calculate the weight of iron necessary to react completely with 2.00 liters of 3.00 molar $SnCl_4$.

A-5 $\dfrac{2.00\ \cancel{liter\ SnCl_4\ solution}}{} \left| \dfrac{3.00\ \cancel{mole\ SnCl_4}}{1\ \cancel{liter\ solution}} \right| \dfrac{1\ \cancel{mole\ Fe}}{1\ \cancel{mole\ SnCl_4}} \left| \dfrac{55.8\ g\ Fe}{1\ \cancel{mole\ Fe}} \right. = 335$ g Fe

S-2 **In an aqueous solution of HCl, the HCl molecule dissociates according to the following equation:**

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

The reaction proceeds to completion and HCl is said to be 100% dissociated in aqueous solution. The water of hydration is usually omitted and the reaction is written as follows:

$$HCl \rightleftharpoons H^+ + Cl^-$$

HCl is called a strong acid because it is 100% dissociated in aqueous solution.

Q-6 Calculate the moles of H^+ and Cl^- ions present in one liter of one molar HCl solution

A-6 $\dfrac{1\ \cancel{\text{mole HCl}}}{1\ \text{liter solution}} \Bigg| \dfrac{1\ \text{mole H}^+}{1\ \cancel{\text{mole HCl}}}$

= 1 mole H^+ per liter of solution

= 1 mole Cl^- per liter of solution

Q-7 Calculate the moles of H^+ present in 200 ml of 1.0 molar HCl solution

A-7 $\dfrac{200\ \cancel{\text{ml solution}}}{} \Bigg| \dfrac{1.0\ \cancel{\text{mole HCl}}}{1000\ \cancel{\text{ml solution}}} \Bigg| \dfrac{1\ \text{mole H}^+}{1\ \cancel{\text{mole HCl}}} = 0.20\ \text{mole H}^+$

Q-8 Calculate the moles of H^+ in 50 ml of 0.10 molar HCl.

A-8 $\dfrac{50\ \cancel{\text{ml solution}}}{} \Bigg| \dfrac{0.10\ \cancel{\text{mole HCl}}}{1000\ \cancel{\text{ml solution}}} \Bigg| \dfrac{1\ \text{mole H}^+}{1\ \cancel{\text{mole HCl}}}$

= 0.0050 mole H^+

= 5.0×10^{-3} mole H^+

Q-9 If NaOH is 100% dissociated to Na^+ ions and OH^- ions in aqueous solution, calculate the moles of hydroxide ion, OH^-, in one liter of 1.0 molar NaOH solution.

A-9 $NaOH \rightleftharpoons Na^+ + OH^-$

$\dfrac{1\ \cancel{\text{liter solution}}}{} \Bigg| \dfrac{1\ \cancel{\text{mole NaOH}}}{1\ \cancel{\text{liter solution}}} \Bigg| \dfrac{1\ \text{mole OH}^-}{1\ \cancel{\text{mole NaOH}}} = 1\ \text{mole OH}^-$

Q-10 Calculate the moles of OH^- in 500 ml of 0.10 molar NaOH solution.

A-10 $\dfrac{500\ \cancel{\text{ml solution}}}{} \Bigg| \dfrac{0.10\ \cancel{\text{mole NaOH}}}{1000\ \cancel{\text{ml solution}}} \Bigg| \dfrac{1\ \text{mole OH}^-}{1\ \cancel{\text{mole NaOH}}} = 0.050\ \text{mole OH}^-$

Q-11 Calculate the moles of OH^- ion in 20 ml of 0.0010 molar NaOH solution.

A-11 $\dfrac{20\ \cancel{\text{ml solution}}}{} \Bigg| \dfrac{0.0010\ \cancel{\text{mole NaOH}}}{1000\ \cancel{\text{ml solution}}} \Bigg| \dfrac{1\ \text{mole OH}^-}{1\ \cancel{\text{mole NaOH}}} = 2.0 \times 10^{-5}\ \text{mole OH}^-$

S-3 When aqueous solutions of HCl and NaOH are mixed, the reaction that occurs is called a neutralization reaction (reaction of an acid and a base) and is written as follows:

$$H^+ + OH^- \rightleftharpoons H_2O$$

(Na^+ and Cl^- ions are omitted because they do not participate in the reaction.)

It is possible to calculate the volume of acid and base necessary for complete neutralization if the concentrations of the acid and base are known. Molarity is the concentration unit used in these calculations.

Q-12 How many moles of HCl are needed to react completely with 35 ml of a 0.20 molar NaOH solution?

A-12 $$35\,\cancel{\text{ml NaOH solution}} \times \frac{0.20\,\cancel{\text{mole NaOH}}}{1000\,\cancel{\text{ml solution}}} \times \frac{1\text{ mole HCl}}{1\,\cancel{\text{mole NaOH}}} = 7.0 \times 10^{-3}\text{ mole HCl}$$

Q-13 What volume of 0.10 molar HCl solution would be needed to provide the moles of HCl calculated in A-12?

A-13 $$7.0 \times 10^{-3}\,\cancel{\text{mole HCl}} \times \frac{1\,\cancel{\text{liter solution}}}{0.10\,\cancel{\text{mole HCl}}} \times \frac{1000\text{ ml}}{1\,\cancel{\text{liter solution}}} = 70\text{ ml}$$

Q-14 Calculate the volume of 0.20 molar HCl needed to react completely with 65 ml of 0.30 molar NaOH solution.

A-14 $$65\,\cancel{\text{ml NaOH solution}} \times \frac{0.30\,\cancel{\text{mole NaOH}}}{1000\,\cancel{\text{ml solution}}} \times \frac{1\,\cancel{\text{mole HCl}}}{1\,\cancel{\text{mole NaOH}}} \times \frac{1000\text{ ml HCl solution}}{0.20\,\cancel{\text{mole HCl}}}$$

= 98 ml of HCl solution

Q-15 Given the following equation.

$$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$

Calculate the volume of 0.50 molar HCl solution needed to react completely with 100 ml of 0.20 molar $Ba(OH)_2$ solution.

A-15 $$1000\,\cancel{\text{ml Ba(OH)}_2\text{ solution}} \times \frac{0.20\,\cancel{\text{mole Ba(OH)}_2}}{1000\,\cancel{\text{ml solution}}} \times \frac{2\,\cancel{\text{mole HCl}}}{1\,\cancel{\text{mole Ba(OH)}_2}} \times \frac{1\,\cancel{\text{liter HCl solution}}}{0.50\,\cancel{\text{mole HCl}}} \times \frac{1000\text{ ml}}{1\,\cancel{\text{liter}}}$$

= 80 ml HCl solution

[redacted]

S-4 One mole of any gas at 0°C and one atmosphere pressure (standard temperature and pressure--STP) occupies 22.4 liters. Therefore, it is possible to calculate the volume of gas produced in a reaction given the balanced equation for the reaction.

Q-16 Given the following equation:

$$2KClO_3 \rightarrow 2KCl + 3O_2(g)$$

What volume of O_2 (at STP) would be produced by 40.0 g of $KClO_3$?

A-16 $$40.0\,\cancel{\text{g KClO}_3} \times \frac{1\,\cancel{\text{mole KClO}_3}}{122\,\cancel{\text{g KClO}_3}} \times \frac{3\,\cancel{\text{mole O}_2}}{2\,\cancel{\text{mole KClO}_3}} \times \frac{22.4\text{ liter O}_2\text{ (STP)}}{1\,\cancel{\text{mole O}_2}} = 11.0\text{ liters at STP}$$

Q-17 According to the equation given in Q-16, what mass of $KClO_3$ would be needed to produce 1.00 liters of O_2 at STP?

A-17 $\frac{1.00\ \cancel{\text{liter } O_2}\text{(STP)}}{} \Big| \frac{1\ \cancel{\text{mole } O_2}}{22.4\ \cancel{\text{liter } O_2}} \Big| \frac{2\ \cancel{\text{mole } KClO_3}}{3\ \cancel{\text{mole } O_2}} \Big| \frac{123\text{ g } KClO_3}{1\ \cancel{\text{mole } KClO_3}} = 3.66\text{ g } KClO_3$

Q-18 Given the following equation

$$6AgNO_3 + AsH_{3(g)} + 3H_2O \rightarrow 6Ag_{(s)} + H_3AsO_3 + 6HNO_3$$

Calculate the volume of arsine, AsH_3, gas at STP needed to react completely with 100 ml of 2.00 molar $AgNO_3$ solution

A-18 $\frac{100\ \cancel{\text{ml } AgNO_3\text{ solution}}}{} \Big| \frac{2.00\ \cancel{\text{mole } AgNO_3}}{1000\ \cancel{\text{ml solution}}} \Big| \frac{1\ \cancel{\text{mole } AsH_3}}{6\ \cancel{\text{mole } AgNO_3}} \Big| \frac{22.4\text{ liter}}{1\ \cancel{\text{mole } AsH_3}\text{(STP)}} = 0.747\text{ liter}$

Q-19 What mass of solid Ag metal would be produced from the reaction described in Q-18

A-19 $\frac{100\ \cancel{\text{ml } AgNO_3\text{ solution}}}{} \Big| \frac{2.00\ \cancel{\text{mole } AgNO_3}}{1000\ \cancel{\text{ml solution}}} \Big| \frac{6\ \cancel{\text{mole Ag}}}{6\ \cancel{\text{mole } AgNO_3}} \Big| \frac{108\text{ g Ag}}{1\ \cancel{\text{mole Ag}}} = 2.16\text{ g Ag metal}$

Q-20 Given the following equation:

$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$

How many moles of gaseous oxygen, O_2, at STP would be needed to produce 1.00 liter of gaseous sulfur dioxide, SO_2, at STP?

A-20 $\frac{1.00\ \cancel{\text{liter } SO_2}}{} \Big| \frac{1\ \cancel{\text{mole } SO_2}}{22.4\ \cancel{\text{liter } SO_2}} \Big| \frac{3\text{ mole } O_2}{2\ \cancel{\text{mole } SO_2}} = 0.0670\text{ mole } O_2$

Q-21 What mass of zinc sulfide, ZnS, would be needed to react completely with 0.0670 mole of O_2 according to the equation in Q-20?

A-21 $\frac{0.0670\ \cancel{\text{mole } O_2}}{} \Big| \frac{2\ \cancel{\text{mole ZnS}}}{3\ \cancel{\text{mole } O_2}} \Big| \frac{97.5\text{ g ZnS}}{1\ \cancel{\text{mole ZnS}}} = 4.35\text{ g ZnS}$

Q-22 Given the following equation:

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 4H_2O + 2NO$$

Calculate the mass of Pb needed to produce 1.00 liter of nitric oxide, NO, at STP.

A-22 $\frac{1.00\ \cancel{\text{liter NO}}}{} \Big| \frac{1\ \cancel{\text{mole NO}}}{22.4\ \cancel{\text{liter NO}}} \Big| \frac{3\ \cancel{\text{mole Pb}}}{2\ \cancel{\text{mole NO}}} \Big| \frac{207\text{ g Pb}}{1\ \cancel{\text{mole Pb}}} = 13.9\text{ g Pb}$

Q-23 Calculate the volume of 0.100 molar nitric acid solution, HNO_3, needed to dissolve completely the mass of lead in the previous problem, 13.9 grams.

A-23
$$\frac{13.9\ \cancel{g\ Pb}}{} \left|\frac{1\ \cancel{mole\ Pb}}{207\ \cancel{g\ Pb}}\right| \frac{8\ \cancel{mole\ HNO_3}}{3\ \cancel{mole\ Pb}} \left|\frac{1\ liter\ HNO_3\ solution}{0.100\ \cancel{mole\ HNO_3}}\right. = 1.79\ liters\ 0.100\ M\ HNO_3$$

PART V: Limiting Reagent and Percent Yield

S-1 For any chemical reaction, the amount of product which may be obtained is limited by the amount of starting material. Even if an excess of one reactant is added, the amount of product formed is determined by the limiting reagent, i.e., the reactant not present in excess.

Q-1 According to the following equation

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2,$$

what mass of Fe_3O_4 could be obtained from 16.7 g of Fe and 20.0 g of water?

(Hint: Determine which reactant is present in excess.)

A-1 First, calculate the amount of water needed to react completely with 16.7 g of Fe.

$$\frac{16.7\ \cancel{g\ Fe}}{} \left|\frac{1\ \cancel{mole\ Fe}}{55.8\ \cancel{g\ Fe}}\right| \frac{4\ \cancel{mole\ H_2O}}{3\ \cancel{mole\ Fe}} \quad \frac{18\ g\ H_2O}{1\ \cancel{mole\ H_2O}} = 7.2\ g\ H_2O$$

Therefore, water is present in excess and the amount of iron present determines the mass of Fe_3O_4 obtained.

$$\frac{16.7\ \cancel{g\ Fe}}{} \left|\frac{1\ \cancel{mole\ Fe}}{55.8\ \cancel{g\ Fe}}\right| \frac{1\ \cancel{mole\ Fe_3O_4}}{3\ \cancel{mole\ Fe}} \left|\frac{231\ g\ Fe_3O_4}{1\ \cancel{mole\ Fe_3O_4}}\right. = 23.1\ g\ Fe_3O_4\ \text{(mass obtained)}$$

Note: If you had first calculated the mass of iron needed to react with 20.0 g of water, you would have found that there wasn't enough iron present and thus determined that water was present in excess.

Q-2 Calculate the mass of NaOH that could be obtained from 15.0 g of Na_2O_2 and 1.80 g of H_2O according to the following equation:

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

A-2 Calculate the mass of H_2O needed to react with 15.0 g of Na_2O_2.

$$\frac{15.0\ \cancel{g\ Na_2O_2}}{} \left|\frac{1\ \cancel{mole\ Na_2O_2}}{78.0\ \cancel{g\ Na_2O_2}}\right| \frac{2\ \cancel{mole\ H_2O}}{2\ \cancel{mole\ Na_2O_2}} \left|\frac{18\ g\ H_2O}{1\ \cancel{mole\ H_2O}}\right. = 3.46\ g\ H_2O\ \text{(mass needed)}$$

Therefore, Na_2O_2 is present in excess and the mass of NaOH obtained is limited by the mass of H_2O reacted.

$$\frac{1.80\ \cancel{g\ H_2O}}{} \left|\frac{1\ \cancel{mole\ H_2O}}{18.0\ \cancel{g\ H_2O}}\right| \frac{4\ \cancel{mole\ NaOH}}{2\ \cancel{mole\ H_2O}} \left|\frac{40.0\ g\ NaOH}{1\ \cancel{mole\ NaOH}}\right. = 8.00\ g\ NaOH\ \text{(mass obtained)}$$

Q-3 According to the following equation

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2,$$

what volume of hydrogen could be obtained at STP from 2.40 g of Al and 200 ml of 3.00 M H_2SO_4?

A-3 Calculate the volume of 3 00 M H_2SO_4 needed to react completely with 2.40 g of Al

$$\begin{array}{l|l|l|l|l} 2\ 40\ \cancel{\text{g Al}} & 1\ \cancel{\text{mole Al}} & 3\ \cancel{\text{mole } H_2SO_4} & 1\ \cancel{\text{liter } H_2SO_4}\text{ solution} & 1000\text{ ml solution} \\ \hline & 27\ 0\ \cancel{\text{g Al}} & 2\ \cancel{\text{mole Al}} & 3\ 00\ \cancel{\text{mole } H_2SO_4} & 1\ \cancel{\text{liter solution}} \end{array}$$

= 44 4 ml (volume 3 00 M H_2SO_4 needed)

Therefore, H_2SO_4 is present in excess and the volume of H_2 gas obtained is determined by the mass of Al present

$$\begin{array}{l|l|l|l} 2\ 40\ \cancel{\text{g Al}} & 1\ \cancel{\text{mole Al}} & 3\ \cancel{\text{mole } H_2} & 22.4\text{ liter } H_2 \\ \hline & 27\ 0\ \cancel{\text{g Al}} & 2\ \cancel{\text{mole Al}} & 1\ \cancel{\text{mole } H_2}\text{ at STP} \end{array} = 2.99\text{ liter } H_2\text{ produced}$$

Q-4 Given the following equation·

$$8KI + 9H_2SO_4 \rightarrow 8KHSO_4 + 4I_2 + H_2S + 4H_2O$$

Calculate the volume of H_2S gas at STP that could be obtained from 133 g KI and 250 ml of 6.00 M H_2SO_4.

A-4 Calculate the volume of 6 00 M H_2SO_4 needed to react completely with 133 g of KI.

$$\begin{array}{l|l|l|l} 133\ \cancel{\text{g KI}} & 1\ \cancel{\text{mole KI}} & 9\ \cancel{\text{mole } H_2SO_4} & 1\text{ liter } H_2SO_4\text{ solution} \\ \hline & 166\ \cancel{\text{g KI}} & 8\ \cancel{\text{mole KI}} & 6.00\ \cancel{\text{mole } H_2SO_4} \end{array} = 0.150\text{ liter } H_2SO_4\text{ solution}$$

Therefore, the H_2SO_4 is present in excess and the volume of H_2S obtained is limited by the amount of KI present.

Calculate the volume of H_2S obtained.

$$\begin{array}{l|l|l|l} 133\ \cancel{\text{g KI}} & 1\ \cancel{\text{mole KI}} & 1\ \cancel{\text{mole } H_2S} & 22.4\text{ liter} \\ \hline & 166\ \cancel{\text{g KI}} & 8\ \cancel{\text{mole KI}} & 1\ \cancel{\text{mole } H_2S}\text{ at STP} \end{array} = 2.24\text{ liter } H_2S$$

[redacted]

S-2 The amount of product which should be obtained in a reaction may be calculated from the balanced equation and the mass of reactants. However, in the laboratory this calculated or theoretical yield of product is seldom obtained. The percent yield of product is calculated according to the following formula:

$$\%\text{ yield} = \frac{\text{mass or volume of product (obtained)}}{\text{mass or volume of product (theoretical)}} \times 100$$

Q-5 In A-56, page 63, the theoretical yield of Fe_3O_4 was 115 g from a given mass of reactants. If a student obtained 90.0 g of Fe_3O_4 using the same mass of reactants, calculate the % yield of the reaction.

A-5 $\quad \% \text{ yield} = \frac{90.0 \text{ g}}{115 \text{ g}} \times 100 = 78.3\%$	Q-6 In A-58, page 63, the theoretical yield of Al_2O_3 from a given mass of reactant was 9.44 g. If a student obtained 6.34 g of Al_2O_3 in the laboratory, calculate the % yield
A-6 $\quad \% \text{ yield} = \frac{6.34 \text{ g}}{9.44 \text{ g}} \times 100 = 67.2\%$	Q-7 In A-16, page 73, the theoretical volume of O_2 gas obtained from a given mass of reactant was 11.0 liters. If a student obtained 8.26 liters, calculate the % yield
A-7 $\quad \% \text{ yield} = \frac{8.26 \text{ liters}}{11.0 \text{ liters}} \times 100 = 75.1\%$	Q-8 In A-3, page 76, the theoretical volume of H_2 gas obtained from a given mass of starting material was 2.99 liters. If a student obtained 2.76 liters, calculate the % yield
A-8 $\quad \% \text{ yield} = \frac{2.76 \text{ liters}}{2.99 \text{ liters}} \times 100 = 92.3\%$	

NOTES

Chapter 3 | *ATOMIC STRUCTURE*

Part I <u>The Nucleus and Nuclear Reactions</u>

After completing this section you should be able to

a) understand nuclear structure and notation
b) understand factors contributing to the stability of a nucleus
c) write nuclear reactions and calculate the energy associated with them.

Part II· <u>Electronic Structure and Spectra</u>

After completing this section you should be able to

a) understand the relationship between energy, wave length, frequency, and wave number
b) explain the origin of absorption and emission spectra
c) understand the difference between the Bohr quantum theory and wave mechanics
d) understand the relationship between quantum numbers and electronic structure.

Part III: <u>Chemical Periodicity</u>

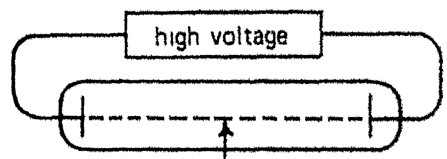
After completing this section you should be able to

a) understand the relationship between electronic structure and the position of the elements in the periodic table
b) predict the relative size and ionization energies of atoms and their magnetic properties.

PART I: The Nucleus and Nuclear Reactions

S-1 The atom is composed of a nucleus and electrons The electron is a negatively charged particle with a mass of 9.10×10^{-28} gram The electric charge of an electron is $-1\ 602 \times 10^{-19}$ coulomb The nucleus is made up of protons and neutrons The proton is a positively charged particle with a mass $1\ 67 \times 10^{-24}$ gram. The charge on the proton is the same as that of the electron, but with an opposite sign The neutron is a particle with no electric charge and a mass of $1\ 67 \times 10^{-24}$ gram. The electrons, which are located outside the nucleus of every atom, occupy an average space much greater than the nuclear volume

Q-1 A discharge tube emits a beam of electrons from a negative electrode to a positive electrode when a high voltage source is placed across these electrodes. This beam of electrons is called a cathode ray.



If an electrically charged plate is placed above and below the cathode ray (the positively charged plate at the top, the negatively charged plate at the bottom), which way will the cathode ray be deflected?

A-1 The beam will be deflected upward because opposite charges attract each other. (Electrons are negatively charged)

Q-2 J. J. Thompson determined the ratio of charge to mass for an electron in coulombs per gram by measuring the deflection of cathode rays in electric and magnetic fields. What value did he find for this ratio?

A-2 $$\frac{-1.602 \times 10^{-19} \text{ coulomb}}{9.10 \times 10^{-28} \text{ gram}} = -1.76 \times 10^{8} \text{ coulomb/g}$$

Q-3 What is the ratio of the mass of an electron to the mass of a proton?

A-3 $$\frac{9.10 \times 10^{-28} \text{ g for electron}}{1.67 \times 10^{-24} \text{ g for proton}} = 5.45 \times 10^{-4} = \frac{1}{1837}$$

Q-4 What conclusion can you draw about the contribution of the mass of the electron to the mass of the atom?

A-4 The mass of an electron may be considered negligible compared to that of the proton and neutron when working with less than 4 significant figures Since all atoms are made up of a nucleus as well as electrons, the contribution of the electrons to the mass of the atom is very small

Q-5 What is the sign of the charge for the nucleus of any atom?

A-5 Since the nucleus is made up of protons and neutrons, it would have a positive charge

Q-6 Ionization is defined as the loss of an electron from an atom What would be the charge of the particle remaining after ionization?

A-6 Since the negative electron is being lost on ionization from a neutral atom, the remaining particle would have a positive charge.

Q-7 Rutherford performed an experiment in which he directed a beam of helium nuclei (called alpha -α- particles) at a thin metal foil. By observing the scattering of these α particles when they went through the foil, he found that most of the particles went directly through the foil without any deflection. However, a few particles were deflected at very large angles. Account for Rutherford's results.

(Hint: An α particle with its positive charge will be deflected from its original path only when it comes very close to the positively charged nucleus.)

A-7 The nuclei occupy only a very small part of the total volume of the foil. The atom consists of a positively charged nucleus of small size and high mass. Most of the alpha particles can go through the thin foil without encountering any of the nuclei of the foil, and consequently, are not deflected. However, a few α particles will come very close to the high concentration of positive charge and mass of a foil nucleus. The nucleus is relatively immovable because of its high mass. As the like charges get closer together, they repel each other, causing the α particle to swerve from its original path.

Q-8 Iron has an atomic weight of 55.8 and a denisty of 7.86 grams per cubic centimeter (cc). What volume does each iron atom occupy?

A-8 $$\frac{55.8\ \cancel{\text{g Fe}}}{1\ \cancel{\text{mole}}} \left| \frac{1\ \cancel{\text{mole}}}{6.02 \times 10^{23}\ \text{atom}} \right| \frac{1\ \text{cc}}{7.86\ \cancel{\text{g Fe}}}$$

$$= 1.18 \times 10^{-23}\ \text{cc/atom}$$

Q-9 If an iron atom is spherical in shape and its volume is 1.18×10^{-23} cc, what is the radius of an iron atom?

($V = 4/3\ \pi r^3$)

A-9 $r^3 = \frac{3(V)}{4\pi}$

$r = \sqrt[3]{\frac{(3)\ (1.18 \times 10^{-23}\ cc)}{4\pi}}$

$= 1.41 \times 10^{-8}$ cm

Q-10 The nucleus of a lead atom has a diameter of approximately 1.0×10^{-13} cm. Lead has an atomic weight of 207.21 and a density of 11.4 grams per cc. If a lead atom is spherical in shape, how many times larger is the diameter of the lead atom than the diameter of the nucleus?

A-10 Calculate the volume of a lead atom

$$\frac{207.21\ \cancel{g\ Pb}}{1\ \cancel{mole\ Pb}} \left| \frac{1\ cc}{11.4\ \cancel{g\ Pb}} \right| \frac{1\ \cancel{mole\ Pb}}{6.02 \times 10^{23}\ atom\ Pb} = 3.01 \times 10^{-23} \frac{cc}{atom\ Pb}$$

Calculate the diameter of a lead atom

$V = \frac{4}{3}\pi r^3 \qquad r = \frac{d}{2}$

$V = \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi \frac{d^3}{8} = \frac{1}{6}\pi d^3$

$d^3 = \frac{6V}{\pi} = \frac{6(3.01 \times 10^{-23}\ cc)}{3.14} = 5.75 \times 10^{-23}$ cc

$d = \sqrt[3]{5.75 \times 10^{-23}\ cc} = 3.86 \times 10^{-8}$ cm

Calculate the ratio of the diameter of the atom to the diameter of the nucleus.

$$\frac{\text{diameter of atom}}{\text{diameter of nucleus}} = \frac{3.86 \times 10^{-8}\ \cancel{cm}}{1.0 \times 10^{-13}\ \cancel{cm}} = 3.9 \times 10^5 = 390{,}000$$

Q-11 The nucleus of a platinum atom has a radius of 5.0×10^{-14} cm. Platinum has an atomic weight of 195.2 and a density of 21.4 grams per cc. If a platinum atom is spherical in shape, how many times larger is the radius of the platinum atom than the radius of the nucleus?

A-11 Calculate the volume of the platinum atom.

$$\frac{195.2\ \cancel{g\ Pt}}{1\ \cancel{mole}} \left| \frac{1\ \cancel{mole}}{6.02 \times 10^{23}\ atom} \right| \frac{1\ cc}{21.4\ \cancel{g\ Pt}} = 1.51 \times 10^{-23}\ cc/atom$$

Calculate the radius of the platinum atom.

$r^3 = \frac{3V}{4\pi} = \frac{3(1.51 \times 10^{-23}\ cc)}{4(3.14)}$

$r = \sqrt[3]{\frac{3(1.51 \times 10^{-23}\ cc)}{4(3.14)}} = 1.53 \times 10^{-8}$ cm

Calculate the ratio of the radius of the atom to the radius of the nucleus.

$$\frac{\text{radius of atom}}{\text{radius of nucleus}} = \frac{1.53 \times 10^{-8}\ \cancel{cm}}{5.0 \times 10^{-14}\ \cancel{cm}} = 3.1 \times 10^5$$

[illegible]

S-2 The atomic number of an element is equal to the number of protons in the nucleus of an atom of the element The atomic number is characteristic of the element (The atomic number of iron is 26.)

The mass number of an atom is an integral number used to indicate the approximate nuclear mass of an atom It is equal to the sum of the number of protons and neutrons in the nucleus These quantities can be represented by writing the chemical symbol as

$$^{A}_{Z}X$$

where X is the symbol for the element, A is the mass number (protons plus neutrons), and Z is the atomic number (protons).

	Q-12 What element has 10 protons in its nucleus?
A-12 Neon, Ne	Q-13 What is the atomic number of Bi?
A-13 83	Q-14 What element has an atomic number of 28?
A-14 Nickel, Ni	Q-15 What is the mass number of oxygen-16?
A-15 16	Q-16 How many protons and neutrons does oxygen-16 contain?
A-16 8 protons and 8 neutrons	Q-17 How many protons and neutrons does lead-207 have? What is the mass number of lead-207?
A-17 82 protons and 125 neutrons mass number = 207	Q-18 Give the atomic symbol for zirconium-91, including values for A and Z.
A-18 $^{91}_{40}Zr$ mass number = 91 atomic number = 40	Q-19 Give the atomic symbol for arsenic-75.
A-19 $^{75}_{33}As$	Q-20 How many protons and neutrons does an element which is represented by the symbol $^{125}_{56}X$ have in its nucleus?
A-20 56 protons and 69 neutrons	[redacted]

S-3 Atoms with different numbers of neutrons but the same number of protons are called isotopes They have the same atomic number but different mass numbers

	Q-21 Give the symbol for another possible isotope of $^{14}_{7}N$
A-21 The atomic number would be the same and the mass number would be different, e g , $^{15}_{7}N$	Q-22 Give the symbol for another possible isotope of $^{28}_{14}Si$
A-22 The atomic number would be the same and the mass number would be different, e g., $^{30}_{14}Si$	

S-4 Atoms with the same mass number but different atomic numbers are called isobars.

	Q-23 Give the symbol for a possible isobar of $^{70}_{31}Ga$
A-23 The atomic number would be different and the mass number the same. $^{70}_{32}Ge$	Q-24 Give the symbol for a possible isobar of $^{113}_{48}Cd$
A-24 The atomic number would be different and the mass number the same. $^{113}_{49}In$	

S-5 Most elements do not exist as a single isotope, but are actually a mixture of isotopes. For example, oxygen is a mixture of isotopes of mass number 16, 17, and 18. The composition of naturally occurring oxygen is

	isotopic mass (actual mass of isotope)
$^{16}_{8}O$ = 99.757%	15.9949
$^{17}_{8}O$ = 0.039%	16.9991
$^{18}_{8}O$ = 0.204%	17.9991

The atomic mass is the average mass of the isotopes as they occur in nature.

For oxygen, atomic mass = (15.9949)(0.99757) + (16.9991)(0.00039 + (17.9991)(0.00204) = 15.999

Q-25 Sulfur exists as four naturally occurring isotopes with mass numbers 32, 33, 34, and 36. Give the atomic symbol for each and the number of protons and neutrons present.

A-25 $^{32}_{16}S$ 16 protons, 16 neutrons

$^{33}_{16}S$ 16 protons, 17 neutrons

$^{34}_{16}S$ 16 protons, 18 neutrons

$^{36}_{16}S$ 16 protons, 20 neutrons

Q-26 Magnesium has three naturally occurring isotopes with isotopic mass and relative abundance of 23.98 (78.60%), 24.98 (10.11%), and 25.98 (11.29%). Find the true mass of the isotopic mixture.

A-26 atomic mass = (23.98)(0.7860) + (24.98)(0.1011) + (25.98)(0.1129) = 24.31

(This is the value that appears on the periodic table.)

Q-27 The element Cd has an atomic mass of 112.40. The most abundant isotope is $^{112}_{48}Cd$. Would other isotopes present in naturally occurring Cd have mass numbers greater, equal to or less than 112?

A-27 greater

Q-28 Calculate the average mass of naturally occurring lithium, Li, if it contains $^{6}_{3}Li$ and $^{7}_{3}Li$ having percentage abundances of 7.40 and 92.60, respectively. The masses of $^{6}_{3}Li$ and $^{7}_{3}Li$ are 6.0167 and 7.0174, respectively.

A-28 atomic mass = (0.0740)(6.0167) + (0.9260)(7.0179) = 6.94

R a) Isotope: same number of protons but different number of neutrons.

b) Isobar: same mass number but different number of protons.

c) Isotopic mass: mass of a particular isotope.

d) atomic mass: average mass of the isotopes as they occur in nature.

S-6 Since the nucleus is made up of neutrons and protons (nucleons), its mass should be equal to the sum of the constituent protons and neutrons. However, when a stable nucleus is formed, the actual mass of the nucleus, M, is always less than the sum of the masses of the nucleons, M'. This difference is known as the mass defect.

$$\Delta M = M' - M$$

This mass defect has been attributed to the packing of nucleons into tiny elements of volume.

Q-29 The isotopic mass is usually expressed in atomic mass units (amu), the mass of an atom relative to the mass of a carbon-12 atom

In calculating the mass defect, the mass of the nucleons must be expressed in the same units as the isotopic mass. The conversion factor is expressed as

$$6.0229 \times 10^{23} \text{ amu} \quad 1 \text{ g}$$

The mass of the proton is 1.6724×10^{-24}g. Calculate the mass of the proton in amu.

A-29 $$\text{mass of proton} = \frac{1.6724 \times 10^{-24}\,\cancel{g}}{} \bigg| \frac{6.0229 \times 10^{23}\text{ amu}}{1\,\cancel{g}} \quad 1.0073 \text{ amu}$$

Q-30 The mass of the neutron is 1.6747×10^{-24} g. Calculate the mass of the neutron in amu.

A-30 $$\text{mass of neutron} = \frac{1.6747 \times 10^{-24}\,\cancel{g}}{} \bigg| \frac{6.0229 \times 10^{23}\text{ amu}}{1\,\cancel{g}} \quad 1.0087 \text{ amu}$$

Q-31 Calculate the mass (in amu) of the nucleons for the helium, $^{4}_{2}He$, nucleus by adding together the masses of the protons and neutrons.

A-31 2 neutrons 2 protons

$M' = 2(1.0073 \text{ amu}) + 2(1.0087 \text{ amu})$

$= 4.0320 \text{ amu}$

Q-32 If the helium nucleus has an actual mass of 4.0015 amu, calculate the mass defect.

A-32 $\Delta M = M' - M$

$\Delta M = 4.0320 \text{ amu} - 4.0015 \text{ amu}$

$= 0.0305 \text{ amu}$

Q-33 What correction must be made to the isotopic mass of the fluorine $^{19}_{9}F$ atom before the mass defect of the fluorine nucleus can be calculated?

A-33 The mass of the electrons must be subtracted from the isotopic mass. This leaves the mass of the fluorine nucleus.

Q-34 What is the mass of an electron in amu? (9.1×10^{-28} g)

A-34 $$\text{mass of electron} = \frac{9.1 \times 10^{-28}\,\cancel{g}}{} \bigg| \frac{6.0229 \times 10^{23}\text{ amu}}{1\,\cancel{g}} = 0.00055 \text{ amu}$$

Q-35 The isotopic mass of fluorine, $^{19}_{9}F$, is 18.9984 amu. What is the mass of the $^{19}_{9}F$ nucleus?

A-35 Fluorine has 9 electrons.

M = mass of $^{19}_{9}F$ nucleus

$= 18.9984 - 9(0.00055)$

$= 18.9984 - 0.0050 = 18.9934 \text{ amu}$

Q-36 If the isotopic mass of aluminum $^{27}_{13}Al$ is 26.9815 amu, what is the mass defect for the aluminum (27) nucleus?

A-36 Aluminum 13 protons
13 electrons
14 neutrons

M = mass of $^{27}_{13}Al$ nucleus
$= 26.9815 - 13(0.00055)$
$= 26.9743$ amu

$M' = 13(1.0073 \text{ amu}) + 14(1.0087 \text{ amu})$
$= 27.2167$ amu

$\Delta M = M' - M = 27.2167 - 26.9743$
$= 0.2424$ amu

Q-37 If the isotopic mass of vanadium $^{51}_{23}V$ is 50.942 amu, what is the mass defect for the vanadium (51) nucleus?

A-37 Vanadium: 23 electrons
23 protons
28 neutrons

$M = 50.942 - 23(0.00055)$
$= 50.929$ amu

$M' = 23(1.0073 \text{ amu}) + 28(1.0087 \text{ amu})$
$= 51.4115$ amu

$\Delta M = M' - M = 51.4115 - 50.929$
$= 0.482$ amu

Q-38 What is the mass defect for arsenic (75) if the isotopic mass is 74.9216 amu?

A-38 Arsenic: 33 electrons
33 protons
42 neutrons

$M = 74.9216 - 33(0.00055)$
$= 74.9035$ amu

$M' = 33(1.0073 \text{ amu}) + 42(1.0087 \text{ amu})$
$= 75.6063$ amu

$\Delta M = M' - M = 75.6063 - 74.9035$
$= 0.7028$ amu

R-7 $\Delta M = M' - M$ where ΔM = mass defect, M' is the mass of the sum of the nucleons, and M is the actual nuclear mass.

S-7 The mass defect is the mass lost in the synthesis of any nucleus from its component particles. This mass is lost in the form of energy. The amount of energy which is equivalent to the loss in mass is given by the Einstein relation

$$E = mc^2$$

The terms are E = energy released
$m = \Delta M$ = mass defect
c = velocity of light (3.00×10^{10} cm/sec)

This energy - equivalent of the mass loss is called the binding energy. The greater the binding energy per nucleon (proton or neutron), the greater the stability of the nucleus. For the problem in Q-38, the amount of energy released in forming one nucleus of arsenic-75 from its component particles (binding energy) can be calculated. The mass defect is 0.7028 amu which corresponds to 1.167×10^{-24} g/nucleus.

$$E = mc^2$$
$$E = (1.167 \times 10^{-24} \text{ g/nucleus})(3.00 \times 10^{10} \text{ cm/sec})^2$$
$$= 1.05 \times 10^{-3} \frac{\text{g-cm}^2}{\text{sec}^2\text{-nucleus}}$$

The energy unit used is the erg

$$\text{erg} = \frac{\text{g-cm}^2}{\text{sec}^2}$$

Therefore,
$$1.05 \times 10^{-3}\ \frac{\text{g-cm}^2}{\text{sec}^2} = 1.05 \times 10^{-3}\ \text{erg}$$

Q-39 Calculate the binding energy for the nucleus of an aluminum atom, given that the mass defect is 0.2424 amu

A-39 mass lost $= \frac{0.2424\ \cancel{\text{amu}}}{\text{nucleus}} \Big| \frac{1\ \text{g}}{6.023 \times 10^{23}\ \cancel{\text{amu}}} = 4.024 \times 10^{-25}$ g/nucleus

$E = (4.024 \times 10^{-25}\ \text{g/nucleus})(3.00 \times 10^{10}\ \text{cm/sec})^2$

$= 3.62 \times 10^{-4} \frac{\text{g-cm}^2}{\text{sec}^2\text{-nucleus}}$

$= 3.62 \times 10^{-4}$ erg/nucleus

Q-40 Calculate the binding energy for the nucleus of a vanadium atom, given that the mass defect is 0.482 amu.

A-40 mass lost $= \frac{0.482\ \cancel{\text{amu}}}{\text{nucleus}} \Big| \frac{1\ \text{g}}{6.023 \times 10^{23}\ \cancel{\text{amu}}} = 8.00 \times 10^{-25}$ g/nucleus

$E = (8.00 \times 10^{-25}\ \text{g/nucleus})(3.00 \times 10^{10}\ \text{cm/sec})^2$

$= 7.20 \times 10^{-4}$ erg/nucleus

Q-41 What is the binding energy for one mole of $^{127}_{53}$I atoms if the mass defect is 1.156 amu/nucleus?

A-41 mass lost $= \frac{1.156\ \cancel{\text{amu}}}{\cancel{\text{nucleus}}} \Big| \frac{1\ \text{g}}{6.023 \times 10^{23}\ \cancel{\text{amu}}} \Big| \frac{6.023 \times 10^{23}\ \cancel{\text{nuclei}}}{\text{mole}} = 1.156$ g/mole

$E = (1.156\ \text{g/mole})(3.00 \times 10^{10}\ \text{cm/sec})^2 = 1.04 \times 10^{21} \frac{\text{g-cm}^2}{\text{sec}^2\text{-mole}}$

$= 1.04 \times 10^{21}$ erg/mole

This is equivalent to the amount of energy needed to raise the temperature of 1,000,000 tons of water 100°C.

Q-42 What is the binding energy for one mole of $^{27}_{13}$Al atoms if the binding energy for one nucleus is 3.62×10^{-4} erg?

A-42 $E = 3.62 \times 10^{-4}$ erg/nucleus

$\frac{3.62 \times 10^{-4}\ \text{erg}}{\cancel{\text{nucleus}}} \Big| \frac{6.023 \times 10^{23}\ \cancel{\text{nuclei}}}{1\ \text{mole}}$

$= 2.18 \times 10^{20}$ erg/mole

Q-43 The binding energy per nucleon (proton or neutron) gives the relative stability of one nucleus to that of another. Calculate the binding energy per nucleon for $^{75}_{33}$As. The binding energy per nucleus is 1.05×10^{-3} erg.

A-43 Arsenic: 33 protons
42 neutrons
75 nucleons

$E = \frac{1.05 \times 10^{-3}\ \text{erg}}{\cancel{\text{nucleus}}} \Big| \frac{1\ \cancel{\text{nucleus}}}{75\ \text{nucleons}}$

$= 1.40 \times 10^{-5}$ erg/nucleon

Q-44 Calculate the binding energy per nucleon for $^{27}_{13}$Al, given that the binding energy per nucleus is 3.62×10^{-4} erg.

A-44 Aluminum: 13 protons
14 neutrons
27 nucleons

$E = \frac{3.62 \times 10^{-4}\ \text{erg}}{\cancel{\text{nucleus}}} \Big| \frac{1\ \cancel{\text{nucleus}}}{27\ \text{nucleons}}$

$= 1.34 \times 10^{-5}$ erg/nucleon

Q-45 Calculate the binding energy per nucleon for $^{127}_{53}$I, given that the binding energy per nucleus is 1.73×10^{-3} erg.

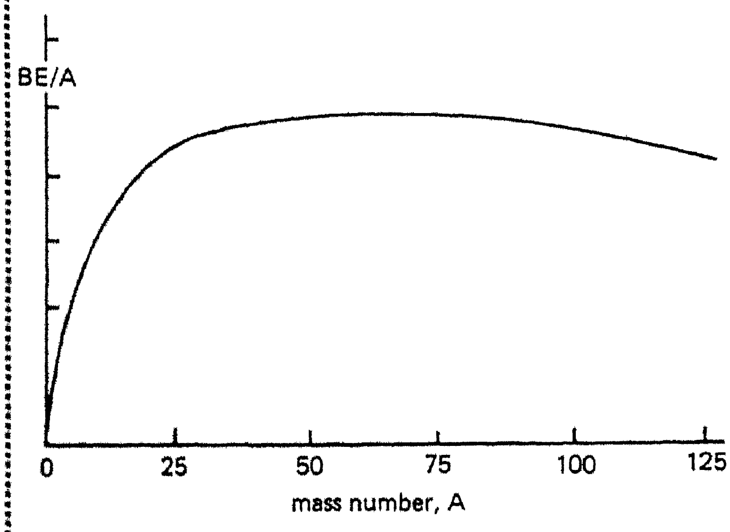
A-45 Iodine: 53 protons
74 neutrons
127 nucleons

$$E = \frac{1.73 \times 10^{-3}\ \text{erg}}{\cancel{\text{nucleus}}} \times \frac{1\ \cancel{\text{nucleus}}}{127\ \text{nucleons}}$$

$$= 1.36 \times 10^{-5}\ \text{erg/nucleon}$$

Q-46 A graph of binding energy per nucleon, BE/A, vs the mass number, A, is given below. Approximately what mass number has the most stable nuclei?

(Hint: Binding energy is equal to the energy lost in forming the nucleus.)



A-46 Since the more stable nuclei have higher binding energy per nucleon, the mass number of the most stable nucleus corresponds to the maximum point on the graph (50-65).

Q-47 Which nucleus would you predict is more stable, Be or Cr?

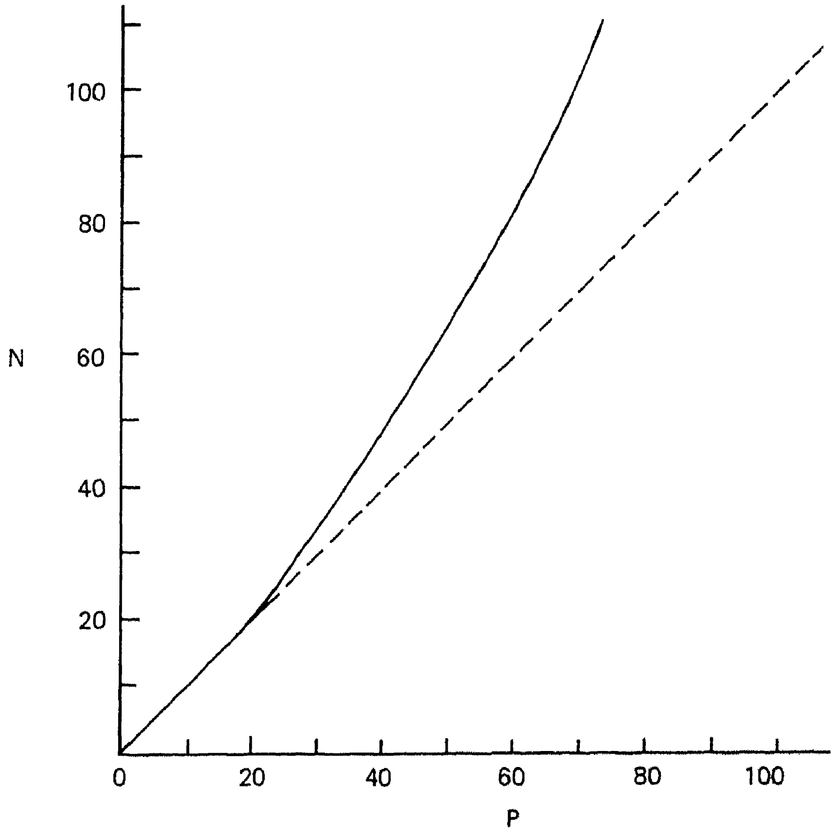
A-47 Cr is more stable than Be. Cr lies higher on the binding energy curve.

Q-48 Which nucleus would you predict is more stable, Ni or I?

A-48 Ni is more stable. Ni lies higher on the binding energy curve.

S-8 Attractive and repulsive forces exist in the nucleus. The attractive forces, which tend to stabilize the nucleus, exist between neutrons and protons, and are due to energy exchange between these particles. The repulsive forces, which decrease the stability of the nucleus, exist between protons because like charges repel each other. The nucleus must reach a balance between these two forces. Since each proton and neutron would be taking part in the energy exchange process, the maximum attractive force should be present when there are equal numbers of protons and neutrons. In a stable nucleus, the number of protons for a given number of neutrons is limited by the repulsive forces. In nuclei containing few protons (atomic number less than 20), the attractive force will predominate. In nuclei containing many protons, the repulsive force will become increasingly important. The relative importance of these two forces is expressed by the neutron to proton ratio (N/P) of the nucleus. This ratio will be approximately one for atomic numbers less than 20, and for atomic numbers greater than 20 it will increase slowly to a value of about 1.5 for atomic number 80. A graph of the number of neutrons vs. the atomic number for stable nuclei is shown on the following page.

To determine the N/P ratio, locate the value of P on the solid line and obtain the corresponding value for N on the y-axis. Divide this value of N by the value of P.



Q-49 Using the graph given in S-8, determine the N/P ratio for the isotope ${}^{12}_{6}C$. What is the actual N/P ratio?

A-49 Carbon has an atomic number less than 20. It should have a N/P ratio of 1 This is true for the isotope ${}^{12}_{6}C$ (6 protons, 6 neutrons)

Q-50 Using the graph given in S-8, determine the N/P ratio for the hafnium isotope ${}^{178}_{72}Hf$. What is the actual N/P ratio?

A-50 From the graph, the value is about 1.5 (${}^{178}_{72}Hf$, 72 protons, 106 neutrons)
The calculated value is 106/72 = 1.47.

Q-51 Using the graph given in S-8, determine the N/P ratio for the xenon isotope, ${}^{124}_{54}Xe$. What is the calculated value?

A-51 From the graph, the value is about 1.3. (${}^{124}_{54}Xe$, 54 protons, 70 neutrons)
The calculated value is 1.30.

Q-52 Where would the value for an unfavorable N/P ratio lie on the graph in S-8?

A-52 It would lie either above or below the solid line on the graph.

Q-53 Would a nucleus with an unfavorable N/P ratio have a high or low binding energy? Why?

A-53 Low binding energy. An unfavorable N/P ratio would mean an unstable nucleus. Since binding energy is a measure of the stability, low stability would mean low binding energy.

S-9 Nuclei with values of N/P that deviate from the solid line on the graph are unstable They become stable by readjusting an unfavorable N/P ratio to a more favorable one This spontaneous process gives rise to the phenomenon called <u>radioactivity</u> The nucleus may lower its N/P ratio by emitting an electron (beta, β, particle) This increases the charge on the nucleus by +1 but does not change the mass number (A neutron can be considered to be made up of an electron and a proton Thus, when an electron is emitted from the neutron, a proton remains. $n \rightarrow p + \beta^-$) Neutron emission would also lower the N/P ratio, but such emissions do not naturally occur

Q-54 What is the symbol for the nucleus remaining after $^{35}_{17}Cl$ undergoes beta emission?

A-54 $^{35}_{18}Ar$

Q-55 What is the symbol for the nucleus remaining after $^{42}_{20}Ca$ undergoes beta emission?

A-55 $^{42}_{21}Sc$

Q-56 What is the symbol for the nucleus remaining after $^{98}_{41}Nb$ undergoes beta emission?

A-56 $^{98}_{42}Mo$

S-10 If necessary, the N/P ratio may be increased by positron emission. A positron is an electron with a positive charge. In effect, a proton emits its positive charge, thus becoming a neutron. Therefore, the emission of a positron changes the charge by -1 but does not change the mass number. ($p \rightarrow n + \beta^+$)

Q-57 What is the symbol for the nucleus remaining after $^{144}_{60}Nd$ undergoes positron emission?

A-57 $^{144}_{59}Pr$

Q-58 What is the symbol for the nucleus remaining after $^{58}_{27}Co$ undergoes positron emission?

A-58 $^{58}_{26}Fe$

S-11 · N/P ratios greater than one may be increased by emission of helium nuclei (which contain two protons and two neutrons) called alpha (α) particles. This emission changes the charge by -2 and the mass by -4.

Q-59 What is the symbol for the nucleus remaining after $^{138}_{56}Ba$ undergoes alpha emission?

A-59 $^{134}_{54}Xe$

Q-60 What is the symbol for the nucleus remaining after $^{120}_{51}Sb$ undergoes alpha emission?

A-60 $^{116}_{49}In$

Q-61 The N/P ratio for a nucleus containing 40 protons is 1.2 Calculate the number of neutrons present in the nucleus

A-61 N/P = 1 2

N/40 = 1 2

N = (1 2)(40) = 48

Q-62 What is the N/P ratio for the nucleus in Q-61 after it undergoes

a) beta emission
b) alpha emission
c) positron emission

A-62 a) N/P = 47/41 = 1 15

b) N/P = 46/38 = 1 21

c) N/P = 49/39 = 1 26

Q-63 A nucleus has a mass number of 155. What is its mass number after alpha emission?

A-63 151

Q-64 A nucleus has an atomic number of 40. What is its atomic number after beta emission?

A-64 41

Q-65 A nucleus has a mass number of 137. What is its mass number after positron emission?

A-65 137

S-12 Particle emission by a nucleus can be written in the form of an equation. For example, beta emission from $^{14}_{6}C$ would be written in the form

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

From this equation it can be seen that the sums of the mass numbers on each side of the arrow are equal for the balanced equation (14 = 14 + 0). The sums of the charges (protons) are also equal (6 = 7 - 1). For alpha emission the equation would be written

$$^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

The sums of the mass numbers on each side of the arrow are equal (226 = 222 + 4). The sums of the charges are also equal (88 = 86 + 2).

Q-66 Write a balanced equation for beta emission from $^{234}_{92}U$.

A-66 ${}^{234}_{92}U \rightarrow {}^{234}_{93}Np + {}^{0}_{-1}e$

Q-67 Write a balanced equation for beta emission from sulfur-36

A-67 ${}^{36}_{16}S \rightarrow {}^{36}_{17}Cl + {}^{0}_{-1}e$

Q-68 Write a balanced equation for positron emission from ${}^{19}_{10}Ne$

A-68 ${}^{19}_{10}Ne \rightarrow {}^{19}_{9}F + {}^{0}_{+1}e$

Q-69 Write a balanced equation for positron emission from magnesium-23

A-69 ${}^{23}_{12}Mg \rightarrow {}^{23}_{11}Na + {}^{0}_{+1}e$

Q-70 Write a balanced equation for alpha emission from ${}^{238}_{92}U$.

A-70 ${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$

Q-71 Write a balanced equation for alpha emission from actinium (Ac-227).

A-71 ${}^{227}_{89}Ac \rightarrow {}^{223}_{87}Fr + {}^{4}_{2}He$

[redacted]

S-13 Just as mass is lost in packing the nuclear particles into a nucleus, mass may be gained or lost in a nuclear transmutation (reaction). The energy associated with this mass is very large ($E = mc^2$). Therefore, nuclear reactions are accompanied by a tremendous absorption or release of energy. This may be indicated by including an energy term, Q, in the equation, as for example

$${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He + Q$$

Q may be positive or negative, depending on whether the reaction is <u>exoergic</u> (positive) or <u>endoergic</u> (negative).

Q-72 When one mole of ${}^{238}_{92}U$ emits alpha particles, 1.0×10^{15} ergs of energy is released. How much energy is lost when 0.50 mole of ${}^{238}_{92}U$ emits alpha particles?

A-72 $$\begin{array}{c|c} 1.0 \times 10^{15}\text{ erg} & 0.50\ \cancel{\text{mole}} \\ \hline 1\ \cancel{\text{mole}} & \end{array}$$

$= 5.0 \times 10^{14}$ erg

Q-73 In the above problem, how much energy is lost when 1.0×10^{6} atoms of ${}^{238}_{92}U$ emit alpha particles?

A-73 $$\begin{array}{c|c|c} 1.0 \times 10^{15}\text{ erg} & 1\ \cancel{\text{mole}} & 1.0 \times 10^{6}\ \cancel{\text{atoms}} \\ \hline 1\ \cancel{\text{mole}} & 6.02 \times 10^{23}\ \cancel{\text{atoms}} & \end{array}$$

$= 1.6 \times 10^{-3}$ erg

Q-74 In the above problem, how much energy is lost when 25.0 grams of ${}^{238}_{92}U$ emit alpha particles?

A-74 $$\begin{array}{c|c|c} 1.0 \times 10^{15}\text{ erg} & 1\ \cancel{\text{mole}} & 25.0\ \cancel{\text{g U}} \\ \hline 1\ \cancel{\text{mole}} & 238\ \cancel{\text{g U}} & \end{array}$$

$= 1.0 \times 10^{14}$ erg

[redacted]

S-14 It is possible to convert one nucleus into another by artificial means Thus, nuclear reactions may be carried out in a manner analogous to chemical reactions The first such reaction observed was that resulting from collisions of nitrogen atoms and alpha particles

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}H$$

In discussing nuclear reactions, it is customary to employ the notation

$$M(a, b)M' ,$$

where M and M' are the starting and product species, respectively, a is the bombarding particle, and b is the emitted particle (if any) Thus, the reaction above may be written

$$^{14}_{7}N\ (\alpha,\ ^{1}_{1}H)^{17}_{8}O\ .$$

Q-75 Write in both nuclear reaction form and shorthand notation an equation to illustrate the reaction of boron-10 with an alpha particle to form nitrogen-13 and a neutron.

A-75 $^{10}_{5}B + ^{4}_{2}He \rightarrow ^{13}_{7}N + ^{1}_{0}n$

$^{10}_{5}B\ (\alpha,\ n)\ ^{13}_{7}N$

Q-76 Write an equation to illustrate the reaction of oxygen-18 with a proton to form fluorine-18 and a neutron, both in nuclear reaction form and in shorthand notation.

A-76 $^{18}_{8}O + ^{1}_{1}H \rightarrow ^{18}_{9}F + ^{1}_{0}n$

$^{18}_{8}O\ (^{1}_{1}H,\ n)\ ^{18}_{9}F$

Q-77 Write an equation to illustrate the reaction of rubidium-85 with a neutron to form krypton-85 plus a proton.

A-77 $^{85}_{37}Rb + ^{1}_{0}n \rightarrow ^{85}_{36}Kr + ^{1}_{1}H$

Q-78 It has been found that in the reaction of nitrogen-14 with an alpha particle to form oxygen and a proton, 1.8×10^{-9} erg of energy are absorbed per nucleus. Write an equation which includes the energy exchange to illustrate the reaction.

A-78 $^{14}_{7}N + ^{4}_{2}He \rightarrow$

$$^{17}_{8}O + ^{1}_{1}H - 1.8 \times 10^{-9}\ \text{erg/nucleus}$$

Q-79 The reaction between two protons and two neutrons to form a helium nucleus is accompanied by a mass loss of 5.0×10^{-26} gram per nucleus formed. Write the nuclear reaction including the energy exchange.

A-79 $E = mc^2$

$$= (5.0 \times 10^{-26}\ \text{g/nucleus})(3.0 \times 10^{10}\ \text{cm/sec})^2$$

$$= 4\ 5 \times 10^{-5} \frac{\text{g-cm}^2}{\text{sec}^2\text{-nucleus}}$$

$$= 4.5 \times 10^{-5}\ \text{erg/nucleus}$$

$$2(^{1}_{1}H) + 2(^{1}_{0}n) \rightarrow ^{4}_{2}He + 4.5 \times 10^{-5}\ \text{erg/nucleus}$$

Q-80 If the reaction of boron-11 with a proton yields carbon-11, what is the other particle given off by the reaction?

A-80 $^{11}_{5}B + ^{1}_{1}H \rightarrow ^{11}_{6}C + \underline{\underline{^{1}_{0}n}}$

Q-81 If in the reaction of fluorine-19 with a neutron, nitrogen-16 is formed, what is the other particle given off in the reaction?

A-81 $^{19}_{9}F + ^{1}_{0}n \rightarrow ^{16}_{7}N + \underline{\underline{^{4}_{2}He}}$

Q-82 Write the nuclear reaction for

$^{14}_{7}N\ (n,\ 2n)\ ^{13}_{7}N$

A-82 $^{14}_{7}N + ^{1}_{0}n \rightarrow ^{13}_{7}N + 2(^{1}_{0}n)$

Q-83 Write the nuclear reaction for

$^{27}_{13}Al\ (?,\ \alpha)\ ^{24}_{12}Mg$.

A-83 $^{27}_{13}Al + ^{1}_{1}H \rightarrow ^{24}_{12}Mg + ^{4}_{2}He$

Q-84 Write the nuclear reaction for

$^{27}_{13}Al\ (\alpha,\ ^{1}_{1}H)$?

A-84 $^{27}_{13}Al + ^{4}_{2}He \rightarrow ^{30}_{14}Si + ^{1}_{1}H$

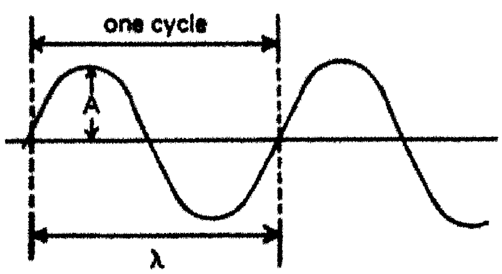
Q-85 Write the nuclear reaction for

$^{12}_{6}C\ (^{2}_{1}H,\ n)\ ^{13}_{7}N$. ($^{2}_{1}H$ = deuterium)

A-85 $^{12}_{6}C + ^{2}_{1}H \rightarrow ^{13}_{7}N + ^{1}_{0}n$

PART II: Electronic Structure and Spectra

S-1 **Since the arrangement of electrons determines the chemical and physical properties of an element, it is extremely important to know the electronic structure of an atom. In this section, spectroscopic observations will be used to construct a model for the atom and to show how this model can explain the chemical and physical properties of the elements. Before considering electronic structure, some properties of light must be understood. Many properties of light can be explained by assuming that light behaves as a wave. A diagram of a wave with its essential features labeled is shown below.**



λ = wave length = distance that the wave moves during one cycle = cm/cycle
A = wave amplitude = the maximum disturbance from the horizontal axis
τ = period = the time for one complete cycle = sec/cycle
ν = frequency of oscillation = the number of cycles that occur in every second = cycle/sec = $1/\tau$.

When speaking of λ, τ, and ν the word cycle is understood and is not a unit of measure. Thus, λ is measured in cm, τ is measured in sec, and ν is measured in sec^{-1}.

Q-1 If a wave has a period, τ, of 0.005 seconds, what is its frequency?

A-1 $\nu = \frac{1}{\tau} = \frac{1}{0.005 \text{ sec}} = 2.0 \times 10^2 \text{ sec}^{-1}$

Q-2 If a wave has a frequency of $1 \times 10^8 \text{ sec}^{-1}$, what is its period?

A-2 $\tau = \frac{1}{\nu} = \frac{1}{1 \times 10^8 \text{ sec}^{-1}} = 1 \times 10^{-8} \text{ sec}$

Q-3 If a wave has a period, τ, of 2.0×10^{-6} sec, what is its frequency?

A-3 $\nu = \frac{1}{\tau} = \frac{1}{2.0 \times 10^{-6} \text{ sec}} = 5.0 \times 10^5 \text{ sec}^{-1}$

R $\nu = \frac{1}{\tau}$, where ν is the frequency of the wave and τ is its period.

S-2 The relationship between wave length (λ) and frequency (ν) for a light wave is given by the equation

$$\lambda\nu = c$$

where c is the velocity of light (3.0×10^{10} cm/sec).

Q-4 The frequency of a wave of light is $1.0 \times 10^6 \text{ sec}^{-1}$. What is the wave length for this wave?

A-4 $\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{10} \text{ cm}}{\cancel{\text{sec}}} \Big| \frac{\cancel{\text{sec}}}{1 \times 10^6}$

$= \frac{3.0 \times 10^{10} \text{ cm}}{1.0 \times 10^6} = 3.0 \times 10^4 \text{ cm}$

Q-5 If the wave length of a certain wave of light is 2.0×10^3 cm, what is the frequency of this wave?

A-5 $\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \cancel{\text{cm}}}{\text{sec}} \Big| \frac{}{2.0 \times 10^3 \cancel{\text{cm}}}$

$= 1.5 \times 10^7 \text{ sec}^{-1}$

Q-6 The wave length of green light is about 5×10^{-5} cm. What would the wave length be in Angstrom units (Å) if $1 \text{ Å} = 1 \times 10^{-8}$ cm?

A-6 $5 \times 10^{-5} \cancel{\text{cm}} \Big| \frac{1 \text{ Å}}{10^{-8} \cancel{\text{cm}}} = 5000 \text{ Å}$

Q-7 If the wave length of green light is about 5000 Å, what is its frequency?

A-7 $\nu = \frac{c}{\lambda}$

$= \frac{3.0 \times 10^{10} \cancel{\text{cm}}}{\text{sec}} \Big| \frac{}{5000 \cancel{\text{Å}}} \Big| \frac{1 \cancel{\text{Å}}}{10^{-8} \cancel{\text{cm}}}$

$= 6.0 \times 10^{14} \text{ sec}^{-1}$

Q-8 If the period of a light wave is 2.0×10^{-10} sec, what is the length of this wave in Angstrom units?

A-8 $\nu = \frac{1}{\tau} = \frac{1}{2.0 \times 10^{-10} \text{ sec}} = 5.0 \times 10^9 \text{ sec}^{-1}$

$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{10} \cancel{\text{cm}}}{\cancel{\text{sec}}} \Big| \frac{\cancel{\text{sec}}}{5.0 \times 10^9} \Big| \frac{1 \text{ Å}}{10^{-8} \cancel{\text{cm}}} = \frac{3 \times 10^{10} \text{ Å}}{(5.0 \times 10^9)(10^{-8})} = 6.0 \times 10^8 \text{ Å}$

[redacted]

S-3 Light can also be regarded as being corpuscular Instead of an oscillating wave as described previously, light can be considered a stream of energy packets or particles traveling with a high velocity (3.0×10^{10} cm/sec) These energy packets are called photons Some physical properties of light are best explained by the wave nature of light and others are best explained by the particle nature. Thus, light is said to be dualistic in nature The theory used is that which best pertains to a particular experiment. The frequency (ν) of the wave theory of light can be related to the energy packets (E) of the particle theory of light through Planck's equation·

$$E = h\nu$$

where h is Planck's constant, a proportionality factor whose value is 6.63×10^{-27} erg-sec (erg = g - cm^2/sec^2)

Q-9 Find the energy of the photons which corresponds to light of frequency 3.0×10^{15} sec^{-1}.

A-9 $E = h\nu = \dfrac{6.63 \times 10^{-27}\ \text{erg-}\cancel{\text{sec}}}{} \Big| \dfrac{3.0 \times 10^{15}}{\cancel{\text{sec}}}$

$= 2.0 \times 10^{-11}$ erg

Q-10 Find the frequency of light that corresponds to photons of energy 5.0×10^{-5} erg.

A-10 $\nu = \dfrac{E}{h} = \dfrac{5.0 \times 10^{-5}\ \cancel{\text{erg}}}{6.63 \times 10^{-27}\ \cancel{\text{erg}}\text{-sec}}$

$= 7.5 \times 10^{21}$ sec^{-1}

Q-11 From the equation for energy, $E = h\nu$ and $\lambda\nu = c$, relate energy to wave length.

A-11 $E = h\nu \qquad \nu = \dfrac{c}{\lambda}$

$E = h\dfrac{c}{\lambda}$

Q-12 Calculate the wave length of light that has the energy 2.6×10^{-12} erg.

A-12 $E = \dfrac{hc}{\lambda} \qquad \lambda = \dfrac{hc}{E}$

$= \dfrac{6.63 \times 10^{-27}\ \cancel{\text{erg-sec}}}{2.6 \times 10^{-12}\ \cancel{\text{erg}}} \Big| \dfrac{3.0 \times 10^{10}\ \text{cm}}{\cancel{\text{sec}}}$

$= 7.6 \times 10^{-5}$ cm $= 7600$ Å

Q-13 What is the energy of photons with wave length = 0.50 Å ?

A-13 $E = h\nu = \dfrac{hc}{\lambda}$

$E = \dfrac{6.63 \times 10^{-27}\ \text{erg-}\cancel{\text{sec}}}{0.50 \times 10^{-8}\ \cancel{\text{cm}}} \Big| \dfrac{3.0 \times 10^{10}\ \cancel{\text{cm}}}{\cancel{\text{sec}}}$

$= 4.0 \times 10^{-8}$ erg

S-4 **Wave number, $\overline{\nu}$, is a wave characteristic that is proportional to energy and is defined as the number of waves per centimeter.**

$$\overline{\nu} = \frac{1}{\lambda}$$

Q-14 **Show that $\overline{\nu}$ is proportional to energy.**

A-14 $E = h\nu$ and $\nu = \frac{c}{\lambda}$

Therefore, $E = hc\frac{1}{\lambda}$

Since $\frac{1}{\lambda} = \overline{\nu}$, $E = (hc)\overline{\nu}$

hc = constant

Q-15 What is the wave number for light with a wave length of 2.0×10^{10} cm ?

A-15 $\overline{\nu} = \frac{1}{\lambda} = \frac{1}{2.0 \times 10^{10}\,\text{cm}} = \frac{5.0 \times 10^{-11}}{\text{cm}}$

Q-16 What is the wave number for light with a wave length of 4000 Å ?

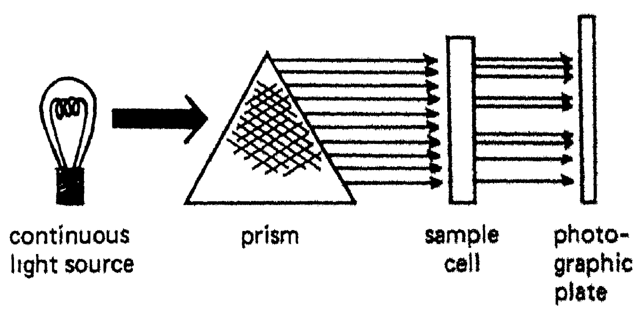
A-16 $\overline{\nu} = \frac{1}{\lambda} = \frac{1}{4000\,\cancel{\text{Å}}} \cdot \frac{1\,\cancel{\text{Å}}}{10^{-8}\,\text{cm}} = 2.5 \times 10^{4}\,\text{cm}^{-1}$

Q-17 What is the energy of photons that corresponds to a wave number of 2.5×10^{-5} cm^{-1}?

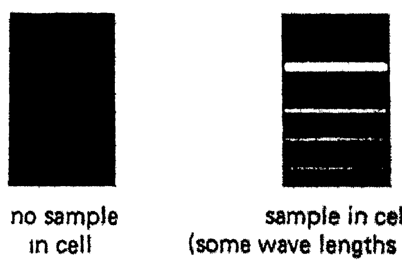
A-17 $E = (hc)\overline{\nu}$

$$= \frac{6.63 \times 10^{-27}\,\text{erg-}\cancel{\text{sec}}}{} \cdot \frac{3 \times 10^{10}\,\cancel{\text{cm}}}{\cancel{\text{sec}}} \cdot \frac{2.5 \times 10^{-5}}{\cancel{\text{cm}}} = 5.0 \times 10^{-21}\,\text{erg}$$

S-5 When continuous light (i.e., light which consists of all possible wave lengths within a given range) is passed through a prism, the light is dispersed into its component wave lengths. When these dispersed wave lengths are passed through cells containing samples of atomic vapors, it is found that the emergent light is no longer continuous. Some of the light waves have interacted with the atoms in the cell. The missing wave lengths can be measured by permitting the dispersed beam of light to fall on a photographic plate. This procedure is called absorption spectroscopy and the recorded image is called a spectrum. Absorption spectroscopy is illustrated by the following diagrams:



photographic plates (spectra)



The sequence of missing lines is characteristic of the atoms in the sample cell and differs from the spectrum of any other atom.

Q-18 What reason can you give for the missing wave lengths on the photographic plate obtained in absorption spectroscopy?

A-18 The light must interact with the atoms and be absorbed.

Q-19 What reason can you give for the spectrum of each type of atom being different?

A-19 Each different type of atom interacts differently with light to absorb a specific wave length of light. The wave length absorbed is characteristic of the absorbing atoms.

Q-20 An atom interacts with light by absorbing an amount of energy equivalent to a given wave length of light. If the spectrum of an atom has a line missing at 4000 Å, what energy does this atom absorb?

A-20

$$E = h\nu \qquad \nu = \frac{c}{\lambda}$$

$$E = \frac{hc}{\lambda}$$

$$E = \frac{6.63 \times 10^{-27}\ \text{erg-}\cancel{\text{sec}}}{4000\ \cancel{\text{Å}}} \left| \frac{3.0 \times 10^{10}\ \cancel{\text{cm}}}{\cancel{\text{sec}}} \right| \frac{1\ \cancel{\text{Å}}}{10^{-8}\ \cancel{\text{cm}}} = 5.0 \times 10^{-12}\ \text{erg}$$

Q-21 An atom is known to absorb energy of 3.0×10^{-12} erg. In the spectrum of this atom, where would there be a missing wave length?

A-21

$$E = \frac{hc}{\lambda} \qquad \lambda = \frac{hc}{E}$$

$$= \frac{6.63 \times 10^{-27}\ \cancel{\text{erg-sec}}}{3.0 \times 10^{-12}\ \cancel{\text{erg}}} \left| \frac{3.0 \times 10^{10}\ \cancel{\text{cm}}}{\cancel{\text{sec}}} \right| \frac{1\ \text{Å}}{10^{-8}\ \cancel{\text{cm}}} = 6600\ \text{Å}$$

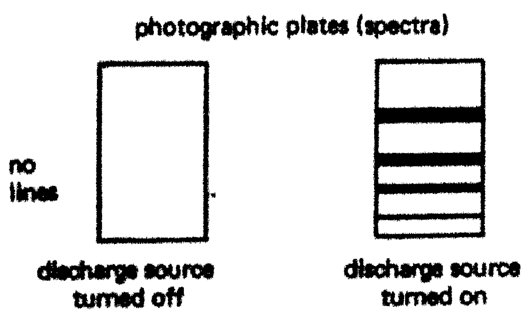
Q-22 An atom is known to absorb energy of 5.0×10^{-11} erg. In the spectrum of this atom, where will there be a missing wave length?

A-22

$$E = \frac{hc}{\lambda} \qquad \lambda = \frac{hc}{E}$$

$$= \frac{6.63 \times 10^{-27}\ \cancel{\text{erg-sec}}}{5.0 \times 10^{-11}\ \cancel{\text{erg}}} \left| \frac{3.0 \times 10^{10}\ \cancel{\text{cm}}}{\cancel{\text{sec}}} \right| \frac{1\ \text{Å}}{10^{-8}\ \cancel{\text{cm}}} = 400\ \text{Å}$$

S-6 Emission spectroscopy is very similar to absorption spectroscopy. Atoms that are subjected to a strong electrical potential will emit a characteristic glow. The light given off by these atoms can be analyzed by allowing the light to pass through a prism and then onto a photographic plate. The photographic plate or spectrum shows lines only at wave lengths of light which are emitted by the atoms in the discharge source.



It is interesting to note that, for a given type of atom, the wave lengths <u>recorded</u> on an emission spectrum are the same as the wave lengths <u>missing</u> on an absorption spectrum

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Q-23 An atom is known to absorb and emit energy equal to 6.0×10^{-11} erg. At what wave length and wave number would a light wave (emission) or a missing light wave (absorption) be obtained in the spectrum?

A-23

$$E = \frac{hc}{\lambda} \qquad \lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.63 \times 10^{-27}\ \cancel{erg}\text{-}\cancel{sec}}{6.0 \times 10^{-11}\ \cancel{erg}} \left| \frac{3.0 \times 10^{10}\ \cancel{cm}}{\cancel{sec}} \right| \frac{1\ \text{Å}}{10^{-8}\ \cancel{cm}} = 330\ \text{Å}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{3.3 \times 10^{-6}\ \text{cm}} = 3.0 \times 10^{5}\ \text{cm}^{-1}$$

Q-24 An atom is known to absorb and emit energy equal to 5.0×10^{-12} erg. At what wave number would you find an emission or absorption line in its spectrum?

A-24

$$E = \frac{hc}{\lambda} = hc\bar{\nu} \qquad \bar{\nu} = \frac{E}{hc}$$

$$\bar{\nu} = \frac{5.0 \times 10^{-12}\ \cancel{erg}}{6.63 \times 10^{-27}\ \cancel{erg}\text{-}\cancel{sec}} \left| \frac{\cancel{sec}}{3.0 \times 10^{10}\ \text{cm}} \right.$$

$$= 2.5 \times 10^{4}/\text{cm} = 2.5 \times 10^{4}\ \text{cm}^{-1}$$

Q-25 The emission spectrum of an atom is found to give a line at 5.0×10^{7} cm^{-1}. What energy does this excited atom emit?

A-25

$$E = \frac{hc}{\lambda} = hc\bar{\nu}$$

$$E = \frac{6.63 \times 10^{-27}\ \text{erg}\text{-}\cancel{sec}}{} \left| \frac{3 \times 10^{10}\ \cancel{cm}}{\cancel{sec}} \right| \frac{5.0 \times 10^{7}}{\cancel{cm}} = 9.9 \times 10^{-9}\ \text{erg}$$

S-7 It has been determined experimentally that the wave number of the individual lines obtained in the emission spectrum of hydrogen atoms fits a mathematical series given by the formula

$$\bar{\nu} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where $\bar{\nu}$ is the observed wave number, R is a constant (called the Rydberg constant) with a value of 109,737 cm^{-1}, and m and n are any integers as long as m is greater than n. The emission spectrum of hydrogen atoms consists of several series of lines. The value of n determines the series to which a given spectral line belongs. In each series, the lines become closer together and reach a limit at m equal to infinity $\left(\frac{1}{m^2} = 0\right)$.

Q-26 In the emission spectrum of hydrogen, the spectral series with n equal to one is called the <u>Lyman series</u> and is observed in the ultraviolet region of the spectrum. Calculate the wave number of the spectral line in this series for a value of m equal to 3.

A-26 $\overline{\nu} = 109,737\ cm^{-1}\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$

$= 109,737\ cm^{-1}\ (1.000 - 0.111)$

$= 109,737\ cm^{-1}\ (0.889) = 9\ 76 \times 10^4\ cm^{-1}$

Q-27 In the emission spectrum of hydrogen, the spectral series with n equal to two is called the Balmer series and is observed in the visible region of the spectrum. Calculate the wave number of the spectral line in this series for a value of m equal to 5

A-27 $\overline{\nu} = 109,737\ cm^{-1}\left(\frac{1}{2^2} - \frac{1}{5^2}\right)$

$= 109,737\ cm^{-1}\ (0.250 - 0.040)$

$= 109,737\ cm^{-1}\ (0.210) - 2.30 \times 10^4\ cm^{-1}$

Q-28 In the emission spectrum of hydrogen, the spectral series with n equal to three is called the Paschen series and is observed in the infrared region of the spectrum. Calculate the wave number for the limit of this series of lines.

A-28 $\lim_{m \to \infty} 1/m^2 = 0$ $\quad \overline{\nu} = 109,737\ cm^{-1}\left(\frac{1}{3^2}\right)$

$= 109,737\ cm^{-1}\ (0.111)$

$= 1.22 \times 10^4\ cm^{-1}$

Q-29 Calculate the wave number for the limit of the series of lines with n = 5.

A-29 $\lim_{m \to \infty} 1/m^2 = 0$ $\quad \overline{\nu} = 109,737\ cm^{-1}\left(\frac{1}{5^2}\right)$

$= 109,737\ cm^{-1}\ (0.040)$

$= 4.39 \times 10^3\ cm^{-1}$

Q-30 Calculate the energy emitted by an excited hydrogen atom which gives a spectral line with values of n and m equal to 3 and 5, respectively.

A-30 $E = hc\overline{\nu} = hc\ (109,737\ cm^{-1})\left(\frac{1}{3^2} - \frac{1}{5^2}\right)$

$= (6.63 \times 10^{-27}\ erg\text{-}\cancel{sec})(3.0 \times 10^{10}\ \cancel{cm/sec})(109,737)(0.111 - 0.040)\ \cancel{cm}^{-1}$

$= 1.55 \times 10^{-12}\ erg$

Q-31 Calculate the energy emitted by an excited hydrogen atom which gives a spectral line in the Balmer series (n = 2) and has a value of m equal to 3.

A-31 Balmer series $n = 2$

$$E = hc\bar{\nu} = hc\ (109{,}737\ cm^{-1})\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= (6\ 63 \times 10^{-27}\ erg\text{-}\cancel{sec})(3\ 0 \times 10^{10}\ \cancel{cm/sec})(109{,}737)(0\ 250 - 0.111)\cancel{cm}^{-1}$$

$$= 3.03 \times 10^{-12}\ erg$$

Q-32 Calculate the energy emitted by an excited hydrogen atom which gives rise to the limiting spectral line in the Lyman series ($n = 1$).

A-32 Lyman series $n = 1$

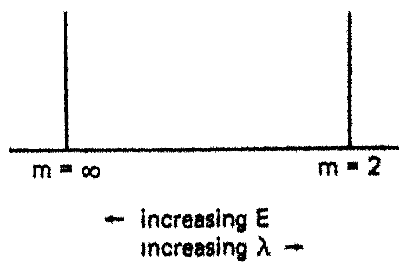
$$\lim_{m \to \infty} 1/m^2 = 0$$

$$E = hc\bar{\nu} = hc\ (109{,}737\ cm^{-1})\left(\frac{1}{1^2}\right)$$

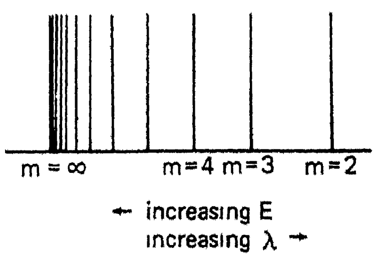
$$= (6\ 63 \times 10^{-27}\ erg\text{-}\cancel{sec})(3\ 0 \times 10^{10}\ \cancel{cm/sec})(109{,}737)\cancel{cm}^{-1}$$

$$= 2\ 18 \times 10^{-11}\ erg$$

Q-33 Sketch the <u>approximate</u> positions of the lines on the energy diagram given below when $m = 3$, $m = 4$, etc. Will the lines be equally spaced?



A-33



S-8 Using the spectral information just considered, Niels Bohr constructed a model for the electrons in atoms that would explain the emission spectrum of the hydrogen atom. He used a new system of mechanics called <u>quantum mechanics</u>. In quantum mechanics, <u>energy is quantized</u>, that is, energy is restricted to having only certain values. Therefore, not all magnitudes of energy are possible. Bohr's model of the atom contained three basic postulates:

1) electrons move in circular orbits around a central nucleus
2) only certain discrete orbits are permitted and the electrons radiate no energy when they are in these orbits
3) a quantum of radiation is emitted or absorbed when an electron jumps from one discrete orbit to another.

Each discrete orbit corresponds to a special energy level. The larger the orbit in which the electron moves, the greater the energy associated with the electron. These energy levels are numbered, starting with the lowest as 1, the next as 2, etc. The number of the energy level, designated by n, is called the principal quantum number. Thus, the energy level with n equal to one is the lowest energy level and the smallest orbit.

Q-34 Consider two hydrogen atoms A and B Hydrogen atom A has an electron with quantum number n = 2 while hydrogen atom B has an electron with n = 4 In which atom is the electron in the largest orbit? Which hydrogen atom has the highest energy?

A-34 The answer is B for both questions. The larger the value for the principal quantum number, the larger is the size of the orbit and the higher is the energy of an electron in this orbit.

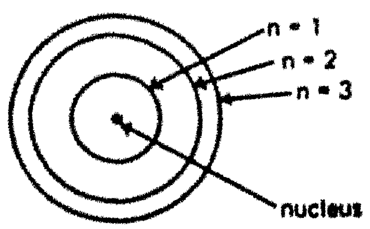
Q-35 What would the principal quantum number be for the electron of the hydrogen atom in its ground state (lowest energy state)?

A-35 n = 1

The ground state would be the state where the electron is in the lowest available energy level.

Q-36 Draw a diagram to illustrate the Bohr picture of an atom. Label each energy level with the correct value of the principal quantum number, n. (It is not necessary to go beyond n = 3.)

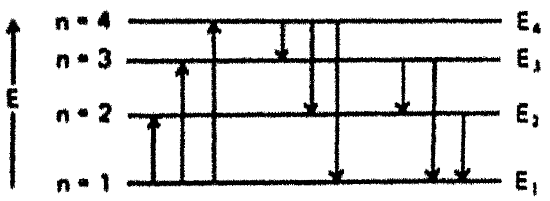
A-36



[redacted]

S-9 An absorption spectrum is produced when light of a certain wave length is absorbed by an atom. The light excites an electron from a lower energy level to a higher energy level. The wave length of light absorbed must be such that the energy ($E = hc/\lambda$) is just equal to the energy difference between the two energy levels.

An emission spectrum is produced when an atom, which has been excited to a higher energy state, spontaneously emits radiation. Below is a diagram of the four lowest energy levels for the hydrogen atom:



The transitions observed in an absorption spectrum are represented by the arrows upward. These transitions correspond to absorption of energy which produces excited hydrogen atoms. The transitions observed in an emission spectrum are represented by the arrows pointing downward. Hydrogen atoms in the excited state with n = 4 can emit light corresponding to the transitions: E_4 to E_3 (4→3), E_4 to E_2 (4→2), and E_4 to E_1 (4→1). After a transition from E_4 to E_3, the same atom may emit light again during a 3→2 or a 3→1 transition. Atoms continue emitting light until they again reach the ground state.

Q-37 In S-7, it was pointed out that the emission spectrum for hydrogen atoms fits the equation.

$$\bar{\nu} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

In order for the wave number to be positive, would n have to be larger or smaller than m?

A-37 $n < m$

(n less than m)

Q-38 A positive wave number corresponds to energy being released When an electron goes from an excited state to a lower energy state, energy is released What are the values for m and n for the transition from $E_4 \rightarrow E_2$?

A-38 $n = 2$

$m = 4$

Q-39 What do the following notations represent?

$3 \rightarrow 1$
$4 \rightarrow 2$
$6 \rightarrow 3$

A-39 $3 \rightarrow 1$ transition from E_3 to E_1

$4 \rightarrow 2$ transition from E_4 to E_2

$6 \rightarrow 3$ transition from E_6 to E_3

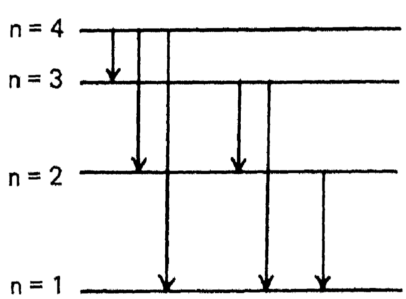
Q-40 What are the values for m and n in the empirical equation for the emission spectrum of hydrogen atoms for each of the transitions in Q-39?

A-40

$3 \rightarrow 1$	$n = 1$	$m = 3$
$4 \rightarrow 2$	$n = 2$	$m = 4$
$6 \rightarrow 3$	$n = 3$	$m = 6$

Q-41 Consider an excited hydrogen atom with an electron in the $n = 4$ energy level. What transitions are possible for this atom to reach the ground state ($n = 1$)? Draw a diagram to help explain.

A-41



The possible transitions are

$4 \rightarrow 1$ $3 \rightarrow 1$ $2 \rightarrow 1$
$4 \rightarrow 2$ $3 \rightarrow 2$
$4 \rightarrow 3$

An emission line corresponding to any one of these transitions could possibly be present

Q-42 An atom emits energy by a $4 \rightarrow 2$ transition. What other transitions must also be present in order to reach the ground state?

A-42 A $2 \rightarrow 1$ transition is the only way that the electron can get to the ground state.

Q-43 If an electron at $n = 4$ emits energy corresponding to a $3 \rightarrow 1$ transition, what other transition must also be present?

A-43 $4 \rightarrow 3$ The electron must get to the $n = 3$ level by some transition in order for the $3 \rightarrow 1$ transition to take place.

Q-44 An atom emits energy by a $4 \rightarrow 3$ transition. What other possible transitions may also be present in order for the electron to reach the $n = 1$ level?

A-44 $3 \to 1$ or $3 \to 2$ and $2 \to 1$

Q-45 What is the energy difference between the n = 1 and n = 2 levels for the hydrogen atom? ($R = 109{,}737\ cm^{-1}$)

A-45 $2 \to 1$ $m = 2$ $n = 1$

$$E = hc\bar{\nu}$$

$$\Delta E_{2,1} = hc\,R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$= (6.63 \times 10^{-27}\ erg\text{-}\cancel{sec})(3.0 \times 10^{10}\ \cancel{cm/sec})(109{,}737)\ \cancel{cm}^{-1}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= 1.64 \times 10^{-11}\ erg$$

Q-46 If an electron drops back from the n = 2 to n = 1 energy level, what is the wave number that would be observed in the emission spectrum for the transition?

A-46

$$\bar{\nu} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$= 109{,}737\left(\frac{1}{1^2} - \frac{1}{2^2}\right)\ cm^{-1}$$

$$= 109{,}737\ (0.750)\ cm^{-1}$$

$$= 8.23 \times 10^4\ cm^{-1}$$

Q-47 What is the energy difference between the n = 2 and n = 3 levels for the hydrogen atom?

A-47 $3 \to 2$ $m = 3$ $n = 2$

$$\Delta E_{3,2} = hc\bar{\nu}$$

$$= (6.63 \times 10^{-27}\ erg\text{-}\cancel{sec})(3.0 \times 10^{10}\ \cancel{cm/sec})(109{,}737)(0.139)\ \cancel{cm}^{-1}$$

$$= 3.03 \times 10^{-12}\ erg$$

Q-48 What is the energy difference between the n = 3 and n = 4 energy levels for the hydrogen atom?

A-48 $4 \to 3$ $m = 4$ $n = 3$

$$\Delta E_{4,3} = hc\bar{\nu}$$

$$= (6.63 \times 10^{-27}\ erg\text{-}\cancel{sec})(3.0 \times 10^{10}\ \cancel{cm/sec})(109{,}737)(0.049)\ \cancel{cm}^{-1}$$

$$= 1.1 \times 10^{-12}\ erg$$

Q-49 From the answers to the last three questions, what can be said about the separation between energy levels as values for n increase?

A-49 The energy differences between two successive energy levels becomes smaller as the value of n increases. Therefore, some limiting value of energy is approached as the value of n becomes very large.

S-10 If an electron obtains more energy than the limiting energy value, the electron escapes from the atom. This process is called ionization and the energy just needed to cause ionization to take place is called the ionization energy

Q-50 For the ground state hydrogen atom, what is the energy necessary to cause ionization? (Hint Calculate $\overline{\nu}$, then E)

A-50 It is the energy needed to take an electron from the n = 1 to the n = ∞ level

$$\overline{\nu} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \qquad n = 1 \qquad m = \infty$$

$$E = h\nu \qquad \nu = \frac{c}{\lambda} \qquad \overline{\nu} = \frac{1}{\lambda}$$

$$= hc\overline{\nu}$$

$$= hc\,(109,737\ \text{cm}^{-1})(1)$$

$$= (6\ 63 \times 10^{-27}\ \text{erg-}\cancel{\text{sec}})(3 \times 10^{10}\ \cancel{\text{cm/sec}})(109{,}737)\cancel{\text{cm}^{-1}}$$

$$= 2\ 18 \times 10^{-11}\ \text{erg}$$

Q-51 What is the ionization energy for an atom with one electron in the n = 2 orbit?

A-51 n = 2 m = ∞

$$E = hc\left(109,737\ \text{cm}^{-1}\right)\left(\frac{1}{2^2}\right)$$

$$= (2\ 18 \times 10^{-11}\ \text{erg})(0\ 25)$$

$$= 5\ 4 \times 10^{-12}\ \text{erg}$$

R **Ionization energy is the energy just needed to cause an electron to escape from the atom.**

S-11 While the Bohr picture of the atom explains the spectra obtained for the hydrogen atom, it does not explain the spectra of any atom that contains more than one electron. The spectra of atoms which contain more than one electron show lines (fine structure) other than those predicted from the Bohr theory The Bohr theory presumed that electrons were in orbits about the nucleus It is not possible to observe whether this is the case since any measurement performed to find the position of the electron will influence the electron so as to change its position Therefore, electrons cannot be assigned to any particular point of space (an orbit) as the Bohr theory presumed. To overcome this difficulty, a new approach called wave mechanics is used to describe the electron in an atom. Wave mechanics is a theory which utilizes the wave properties of particles to construct equations which describe particle motion in terms of probabilities In applying this theory to electrons, the probability equations for motion can be used to relate, mathematically, the energy of particles to the probability of finding the electron at any distance from the nucleus. The allowable energies are obtained in terms of four numbers called quantum numbers. The concepts involved in this theory will be developed over the next several S statements.

In a manner analogous to the dualistic nature of light (particle and wave properties), any moving particle has a wave motion associated with it. The relationship between the velocity and wave length of the particle is expressed mathematically as

$$mv = \frac{h}{\lambda}$$

where m is the mass of the particle, v is its velocity, λ is its wave length, and h is Planck's constant, 6 63 x 10^{-27} erg-sec. (erg = g - cm^2/sec^2)

Q-52 What is the wave length of an electron moving with a velocity of 4.4 x 10^8 cm/sec? (mass of electron = 9.1 x 10^{-28} g)

A-52
$$mv = \frac{h}{\lambda}$$
$$\lambda = \frac{h}{mv}$$
$$\lambda = \frac{(6\ 63 \times 10^{-27}\ \text{erg-sec})}{(9\ 1 \times 10^{-28}\text{g})(4\ 4 \times 10^{8}\ \text{cm/sec})}$$
$$= 1\ 6 \times 10^{-8}\ \frac{\text{erg-sec}^2}{\text{g-cm}}$$
$$\text{erg} = \text{g-cm}^2/\text{sec}^2$$
$$\lambda = 1.6 \times 10^{-8}\ \frac{(\cancel{\text{g}}\text{-cm}^{\cancel{2}}/\cancel{\text{sec}^2})(\cancel{\text{sec}^2})}{\cancel{\text{g-cm}}}$$
$$= 1\ 6 \times 10^{-8}\ \text{cm}$$

Q-53 If the wave length of an electron is 5.0 Å, what is the velocity of the electron?

A-53
$$v = \frac{h}{\lambda m}$$
$$= \frac{(6.63 \times 10^{-27}\ \text{erg-sec})}{(5\ 0 \times 10^{-8}\ \text{cm})(9.1 \times 10^{-28}\text{g})}$$
$$= 1.4 \times 10^{8}\ \frac{\text{erg-sec}}{\text{g-cm}}$$
$$= 1.4 \times 10^{8}\ \frac{(\cancel{\text{g}}\text{-cm}^{\cancel{2}}/\text{sec}^{\cancel{2}})(\cancel{\text{sec}})}{\cancel{\text{g-cm}}}$$
$$= 1.4 \times 10^{8}\ \text{cm/sec}$$

Q-54 What is the wave length of a ball of mass 100 g moving with a velocity of 1.0×10^2 cm/sec?

A-54
$$\lambda = \frac{h}{mv}$$
$$= \frac{(6.63 \times 10^{-27}\ \text{erg-sec})}{(100\ \text{g})(1\ 0 \times 10^{2}\ \text{cm/sec})}$$
$$= 6.6 \times 10^{-31}\ \text{cm}$$

No measuring device is known by which such small waves can be detected or measured. Therefore, the ball does not appear to have wave properties.

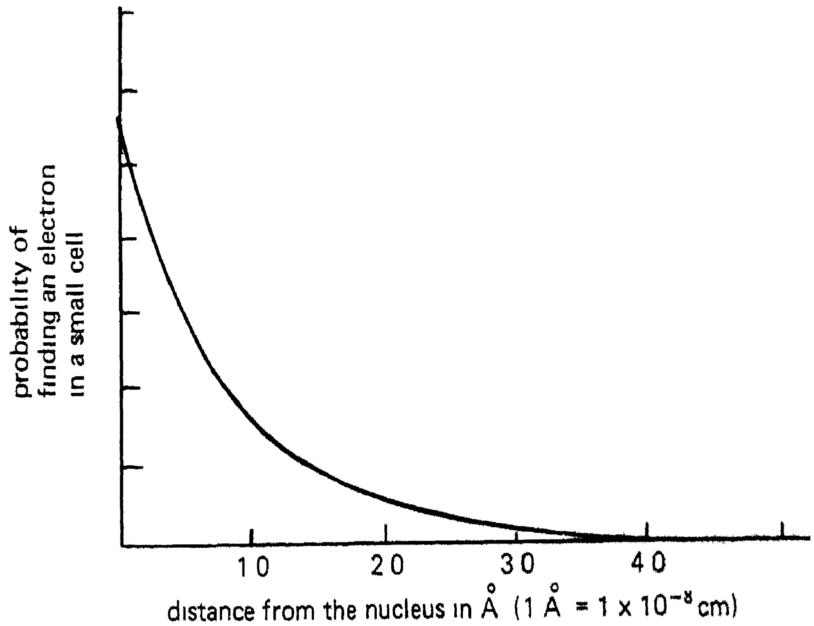
Q-55 What is the wave length of a car with a mass of 1.3×10^6 g moving at a speed of 1.0×10^3 cm/sec?

A-55
$$\lambda = \frac{(6.63 \times 10^{-27}\ \text{erg-sec})}{(1.3 \times 10^{6}\text{g})(1.0 \times 10^{3}\ \text{cm/sec})}$$
$$= 5.1 \times 10^{-36}\ \text{cm}$$

Wave properties are only important for particles of small mass and high velocities.

[redacted]

S-12 Because the position of an electron cannot be determined precisely (Heisenberg uncertainty principle states that it is not possible to measure both the velocity and position of an electron simultaneously), it is best to consider the probability of finding electrons a certain distance from the nucleus By use of wave mechanics, equations have been developed which give the probability of finding an electron within a small cell at various distances from the nucleus The graph below gives this relationship



Q-56 Is the probability of finding an electron in a small cell at a distance of 2Å from the nucleus greater or less than the probability of finding an electron in a cell located 1Å from the nucleus.

A-56 The probability of finding the electron in the cell 1Å from the nucleus is greater

Q-57 Does the probability of finding an electron in a small cell, increase or decrease as the distance of the cell from the nucleus increases.

A-57 The probability decreases with increasing distance of the cell from the nucleus.

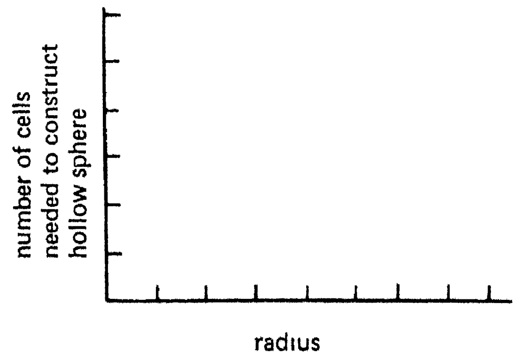
Q-58 Consider two spherical shells constructed from small cells of uniform size such that the nucleus is at the center of the sphere. One shell has a radius of r, and the other has a radius of 2r. Which sphere requires the greater number of small cells for construction.

A-58 The larger sphere (the one with the greater radius) would require the most small cells for construction.

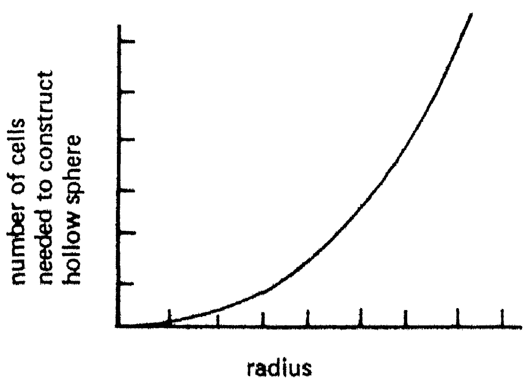
Q-59 Will the number of cells in the larger sphere be exactly twice the number of cells in the smaller sphere? Why? (Hint: Area of sphere equals $4\pi r^2$).

A-59 The number of cells in the larger sphere will be more than twice the number in the smaller sphere The number of cells in the large hollow sphere will be $(2)^2$ or 4 times the number in the small sphere.

Q-60 Sketch on the graph below, a curve which shows the relationship between the radius of a spherical shell and the number of small cells required for its construction

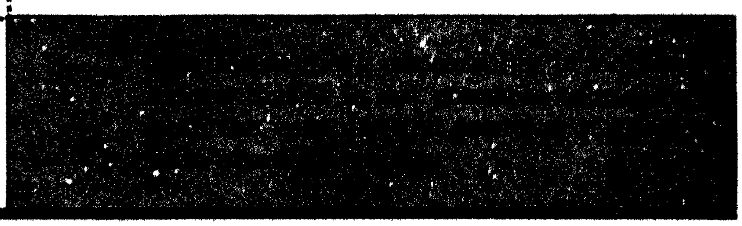


A-60



Q-61 If the probability of finding an electron in a small cell at any distance from the nucleus were the same, how would the probability of finding an electron in a hollow spherical shell made from these small cells change as the radius of the shell increases?

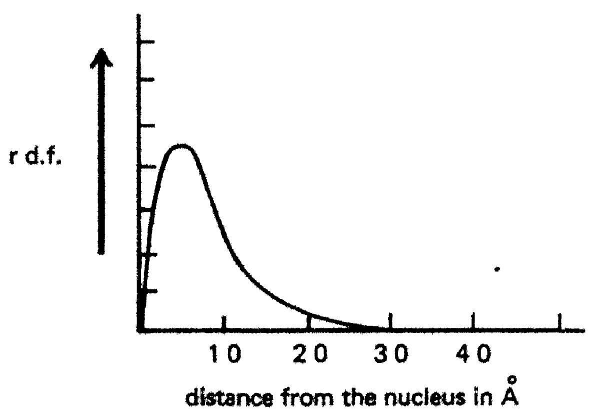
A-61 The probability increases, because there would be more cells in the spherical shell as the radius of the shell increases.



S-13 To determine the probability of locating an electron a certain distance from the nucleus, two factors must be considered:

a) the variation in the probability of finding an electron in a cell at various distances from the nucleus
b) the number of cells in spherical shells at various distances from the nucleus.

To take into account these two factors, a new function is introduced called the radial distribution function which is the product of a and b given above. A plot of this radial distribution function versus the distance from the nucleus for the hydrogen atom is given below.



(Only the general shape of the curve will be of interest.) The most probable place of finding the electron is at the first Bohr radius, but there is also a certain probability of finding the electron at every other distance from the nucleus.

Q-62 From the distribution curve, give the radius which corresponds to the first Bohr orbit

A-62 A maximum in the curve indicates the most probable value, which is the value of the first Bohr orbit Therefore, the radius of the first Bohr orbit is 0 53 Å.

Q-63 According to the Bohr theory, what should the radial distribution function be at a distance from the nucleus equal to 0.3 Å?

A-63 The Bohr theory would say that the electron can only be at 0 53 Å and the probability of it being at any other distance is zero Therefore, the answer is zero In this respect, the Bohr theory and wave mechanical interpretation differ since wave mechanics predicts a finite probability of finding an electron at r = 0 3 Å.

R **The radial distribution function (r. d. f.) gives the probability of finding an electron a certain distance from the nucleus. Probability is used since it is impossible to determine the exact position of the electron.**

S-14 Since the exact position for the electron cannot be given, a charge cloud will be used as a physical picture for the electron in atoms. A line enclosing the region in which the chance (probability) of finding a given electron is greater than one percent gives the shape of the charge cloud

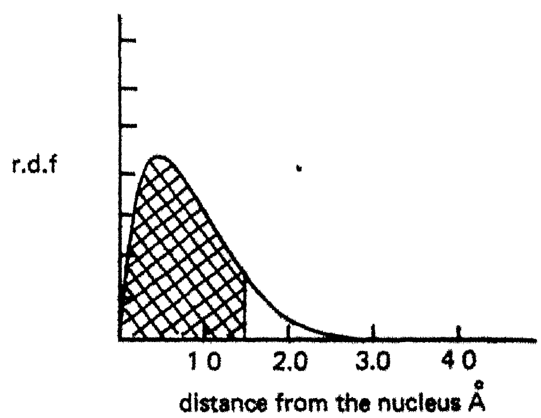
Q-64 What will be the chance (probability) of locating the electron within the boundary of the charge cloud?

A-64 99% chance of locating the electron.

Q-65 If 1000 measurements were made to determine the position of the electron in the atom, how many times would you find the electron within the charge cloud boundary?

A-65 990

Q-66 On the graph of r. d. f. vs distance from the nucleus for the hydrogen atom the region which corresponds to 99 percent chance of finding the electron has been shaded.

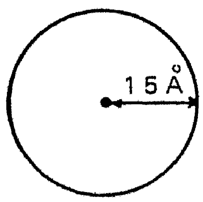


At what distance from the nucleus will the charge cloud boundary be located?

A-66 The region in which there is 99% chance of finding the electron would be at a distance approximately 1 5 Å from the nucleus.

Q-67 Sketch the charge cloud boundary in two dimensions for the electron in the hydrogen atom.
(Hint Probability distribution is spherical about the nucleus)

A-67 The boundary diagram would be spherical with a radius of approximately 1.5 Å Therefore, in two dimensions the boundary diagram would be as follows



R Charge cloud boundaries are used to enclose all the regions in which the chance of finding a given electron is greater than 1 percent.

S-15 Wave equations have been developed that can be applied to particles with wave properties. Solution of these equations yields the explicit mathematical forms for the radial distribution function (r.d.f.) from which the charge cloud boundaries can be determined. Various integer constants arise from these solutions and are given the name quantum numbers. From the solution of these wave equations, it is found that the energy of an atomic state is dependent on the value of an integral parameter, n, in the manner shown below.

$$E \ \alpha \ -\frac{1}{n^2} \qquad (\alpha \text{ means proportional})$$

The energy and the size of the charge cloud of the electron depend on the value of n. The integer, n, is called the principal quantum number and may take on values 1, 2, 3, etc. The radius of the charge cloud is proportional to n^2.

Q-68 Which atom is energetically more stable, one in which the electron has a principal quantum number of 1 or one in which the value is 2? (Hint: The more stable atom has the lower energy.)

A-68 Notice the minus sign in the above equation. E has a lower value (larger negative number) for n = 1. Therefore, this atom is more stable.

Q-69 Which atom has the smaller charge cloud, one in which n = 1 or n = 2?

A-69 n = 1 The electron is held more closely to the nucleus, giving rise to a smaller charge cloud and a more energetically stable configuration. ($r \alpha n^2$)

Q-70 Describe what happens in terms of charge cloud when an atom absorbs energy. (Hint: This energy is absorbed by the electrons.)

A-70 Absorption of energy corresponds to an electron going from a low value of n to a higher value of n. The electron with a higher value of n would have a charge cloud which extends further from the nucleus. Therefore, the excitation would correspond to the transfer of an electron to a more loosely bound location in the atom.

[redacted]

S-16 The atom consists of many energy levels, each of which is related to a particular value of n. Therefore, the principal quantum number defines an energy level in the atom. These levels are sometimes designated by the letters K, L, M, and N to represent the principal quantum numbers 1, 2, 3, and 4, respectively The number of electrons allowed in any one level can be calculated from the equation,

$$\text{maximun number of electrons per energy level} = 2n^2$$

Q-71 What does the value of the principal quantum number characterize in terms of energy and distance?

A-71 The principal quantum number characterizes the average distance of the energy level from the nucleus and characterizes the energy of the level

Q-72 What is the maximum number of electrons permissible in the $n = 2$ energy level?

A-72 $2n^2 = 8$ (maximum number of electrons)

Q-73 What is the maximum number of electrons permissible in the $n = 3$ energy level?

A-73 $2(3)^2 = 18$

Q-74 What is the maximum number of electrons permissible in the $n = 1$ energy level?

A-74 $2(1)^2 = 2$

S-17 It is found from a solution of the equations of wave mechanics that small differences in energy exist for electrons within any one energy level and that the charge cloud distribution for these electrons is not the same. Electrons of different energy within an energy level are assigned to <u>sublevels</u>. These sublevels are characterized by another integral constant, ℓ, called the <u>angular momentum quantum number</u>. The quantum number, ℓ, can have values of 0, 1, 2, 3, . . , n-1 Sublevels are often designated by small letters s, p, d, f, ... which correspond to the angular momentum quantum numbers (ℓ) of 0, 1, 2, 3, ... (the energy of the sublevels increases as the value of ℓ increases). For example, in the $n = 1$ energy level, the only possible value for ℓ is zero. Therefore, in this energy level, all the electrons must be in the $\ell = 0$ or s sublevel.

Q-75 What sublevels are possible in the $n = 2$ energy level?

A-75 $(n-1) = 1$ Therefore, the possible sublevels are
$\ell = 0$ (s sublevel) and
$\ell = 1$ (p sublevel)

Q-76 What sublevels are possible in the $n = 3$ energy level?

A-76 $(n-1) = 2$
$\ell = 0$ (s sublevel)
$\ell = 1$ (p sublevel)
$\ell = 2$ (d sublevel)

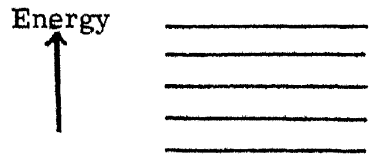
Q-77 What sublevels are possible in the $n = 4$ energy level?

A-77 $(n-1) = 3$
$\ell = 0$ (s sublevel)
$\ell = 1$ (p sublevel)
$\ell = 2$ (d sublevel)
$\ell = 3$ (f sublevel)

Q-78 From your knowledge of sublevels how might the origin of the fine structure (S-11) of spectral lines be explained.

A-78 Since the sublevels are quantized, spectral lines could arise when an electron moves from one sublevel to another in a manner identical with transitions from one energy level to another.

Q-79 Arrange on an energy diagram the relative energy of sublevels for the n = 1, 2, and 3 energy levels.



A-79

n = 3	______	d (3d)
	______	p (3p)
	______	s (3s)
n = 2	______	p (2p)
	______	s (2s)
n = 1	______	s (1s)

The various sublevels are written with their principal quantum number before them to indicate to which energy level they belong. This abbreviated nomenclature is a method for describing the sublevel.

Q-80 Describe the sublevel in the n = 3 energy level with $\ell = 2$. Use abbreviated nomenclature.

A-80 3d sublevel

Q-81 Describe the sublevel in the n = 2 energy level with $\ell = 0$.

A-81 2s sublevel

Q-82 Describe the sublevel in the n = 4 energy level with $\ell = 3$.

A-82 4f sublevel

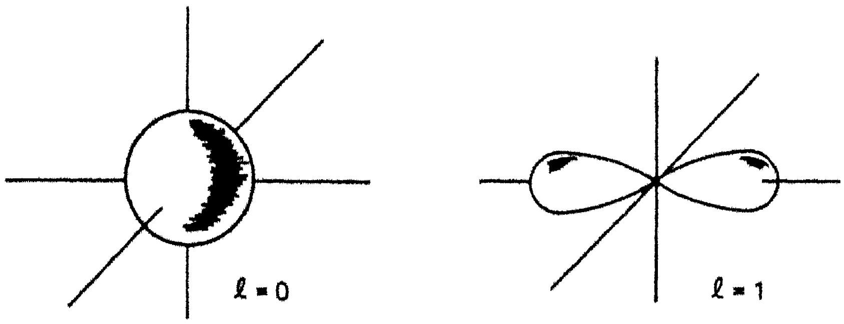
S-18 The charge cloud distribution for electrons within a sublevel is called an orbital. Each sublevel (s, p, d, f) has $2(\ell) + 1$ possible, equivalent orbitals. Each of these $2(\ell) + 1$ orbitals is defined by a quantum number m, where m can have the values of $-\ell, \ldots, -2, -1, 0, +1, +2, \ldots, +\ell$. This quantum number, m, is called the magnetic or orientation quantum number. For $\ell = 1$, there would be three identical orbitals with m = -1, 0, and +1. The orbitals within a given sublevel are given the same letter designation (s, p, d, f) as the sublevel. Thus, the orbitals in the p sublevel are called p orbitals.

	Q-83 Give the number of identical s orbitals in a given energy level and the value for their m quantum number
A-83 For an s orbital, $\ell = 0$ Since the number of orbitals is $2(\ell) + 1$, the number of identical s orbitals must be $2(0) + 1 = 1$ Therefore, m = 0	Q-84 Give the number of identical p orbitals in a given energy level and the values for their m quantum numbers.
A-84 For a p orbital, $\ell = 1$ Since the number of orbitals is $2(\ell) + 1$, the number of identical p orbitals must be 3 Therefore, m = -1, 0, and +1	Q-85 Give the number of identical d orbitals in a given energy level and the values for their m quantum numbers
A-85 For a d orbital, $\ell = 2$ Since the number of orbitals is $2(\ell) + 1$, the number of identical d orbitals must be 5 Therefore, m = -2, -1, 0, +1, +2	Q-86 Give the number of identical f orbitals in a given energy level and the values for their m quantum numbers.
A-86 For the f orbital, $\ell = 3$ $2(3) + 1 = 7$ Therefore, m = -3, -2, -1, 0, +1, +2, +3	Q-87 What is the first energy level that can contain d orbitals?
A-87 For a d orbital, $\ell = 2$ The largest value of ℓ in an energy level is n - 1 Therefore, n would have to be equal to 3	Q-88 For the n = 1 energy level, how many orbitals (of all kinds) are possible?
A-88 One s orbital, total of 1	Q-89 For the n = 2 energy level, how many orbitals (of all kinds) are possible?
A-89 One s orbital + three p orbitals = total of four orbitals.	Q-90 For the n = 3 energy level, how many orbitals (of all kinds) are possible?
A-90 One s orbital + three p orbitals + five d orbitals = total of nine orbitals.	Q-91 In A-88, it was found that the n = 1 energy level contains one s orbital. Remembering that the number of electrons in an energy level is equal to $2n^2$, determine the number of electrons in the 1s orbital.
A-91 The first energy level (n = 1) contains $2(1)^2 = 2$ electrons. It was found in A-88 that there is only one available orbital. Therefore, there must be two electrons per orbital.	**Q-92 Each orbital, regardless of type, can contain the same total number of electrons. How many electrons are contained in each orbital of n = 3 energy level.**

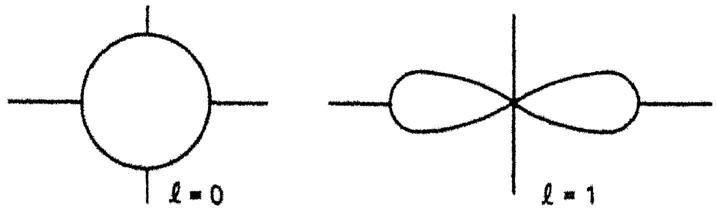
A-92 $n = 3$, $2(3^2) = 18$ total electrons
A-90 gives 9 total orbitals. Therefore, the maximum number of electrons per orbital must be two.

R
a) The number of each kind of orbital in a given energy level is equal to $2(\ell) + 1$.
b) Each equivalent orbital is defined by the magnetic quantum number, m, where m can have the values $-\ell \ldots 0 \ldots +\ell$.
c) Each orbital can contain two electrons.

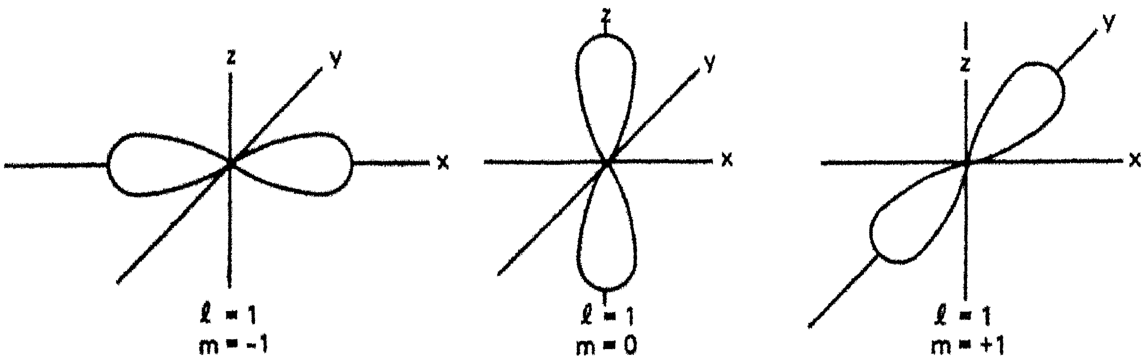
S-19 Orbitals with a given ℓ value have the same shape. The shape of the orbitals with $\ell = 0$ and $\ell = 1$ are given below.



Two dimensional diagrams of the orbitals are shown below.



The different values of m indicate different spatial orientations of the orbitals. For the p orbitals ($\ell = 1$) the orientations can be illustrated as



Q-93 What is the symmetry for an orbital with $\ell = 0$?

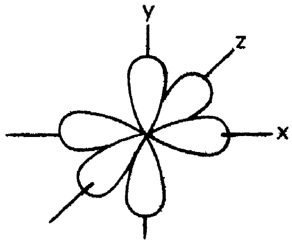
A-93 The charge cloud is symmetrical about the nucleus.

Q-94 What is the symmetry for an orbital with $\ell = 1$?

A-94 The charge cloud is symmetrical about one of the three principal axes of Cartesian coordinates.

Q-95 In a given sublevel with three orbitals of $\ell = 1$, the orbitals are perpendicular to one another. Draw a diagram to illustrate these orbitals.

A-95 Three $\ell = 1$ orbitals each perpendicular to one another



Q-96 What is the difference between the size and shape of a 2p and a 3p orbital?

A-96 The shapes of the orbitals are the same, but a 3p orbital is larger than a 2p orbital

Q-97 Is there any difference between the energy of an electron in orbitals represented by the quantum numbers

$n = 3,\ \ell = 2,\ m = +2$ and $n = 3,\ \ell = 2,\ m = -1$?

A-97 No All orbitals with the same principal and angular momentum quantum numbers have the same energy

Q-98 When an atom is placed in a magnetic field, more spectral lines are observed than in the absence of a magnetic field. This appearance of additional lines is referred to as the Zeeman effect. What gives rise to these new lines? (Hint: In a magnetic field, orbitals with the same value of ℓ are no longer identical in energy.)

A-98 When an atom is placed in a magnetic field, the orbitals of the same kind are no longer identical in energy because some are parallel to the magnetic field while others are not The additional lines arise from electrons being excited from one of these orbitals to another These additional spectral lines are only observed when the atom is in a magnetic field. At all other times, atomic orbitals with the same value of n and ℓ are identical in energy.

[redacted]

S-20 The radial distribution function for the hydrogen atom was developed in S-12 and S-13. The distribution given was for the hydrogen atom with an electron in the lowest energy level, $n = 1$, $\ell = 0$ (the 1s orbital). The r d.f. is a function of the two quantum numbers, n and ℓ. The r d f vs distance from the nucleus for s orbitals in the first three energy levels of the hydrogen atom is given below

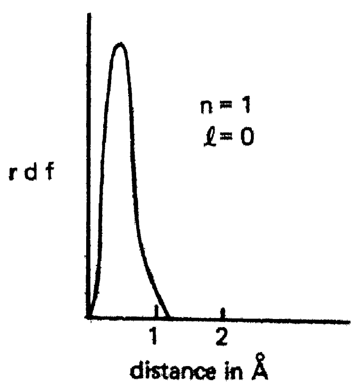


Figure I

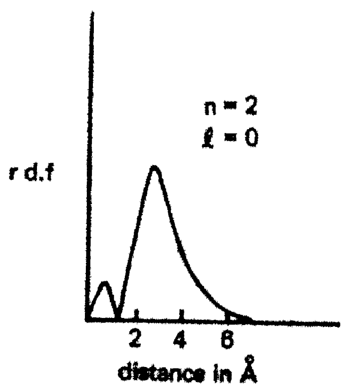


Figure II

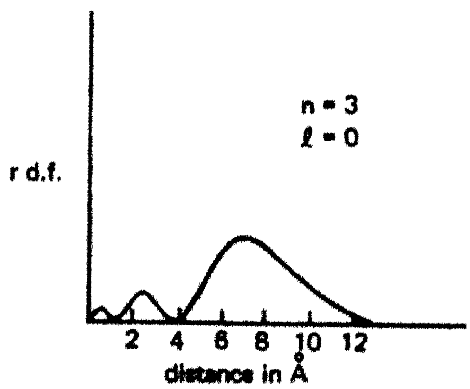


Figure III

Q-99 Figure I represents the probability of finding an electron in the 1s orbital of the H atom. At what distance is there the greatest probability of finding this electron?

A-99 0.53 Å

Q-100 Figure II represents the probability of finding an electron in the 2s orbital of the H atom. At what distance is there the greatest probability of finding an electron in the 2s orbital?

A-100 2.7 Å

Q-101 Figure III represents the probability of finding an electron in the 3s orbital of the H atom. At what distance is there the greatest probability of finding an electron in the 3s orbital?

A-101 6.9 Å

Q-102 With increasing values of n for the s orbital, how does the distance at which there is the greatest probability of finding an electron vary?

A-102 As the energy level increases, the distance of greatest probability increases.

n	distance - Å
1	0.53
2	2.7
3	6.9

Q-103 According to Figure II, what would be the estimated radius of the second Bohr orbit for the hydrogen atom.

A-103 2.7 Å

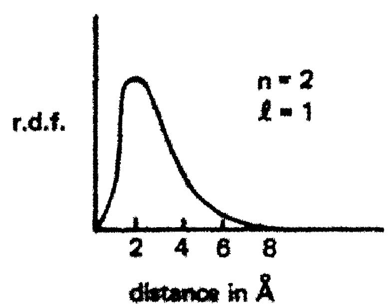
Q-104 According to the Bohr theory, what would be the probability of locating an electron in the n = 2 orbit at a radius of 0.53 Å ?

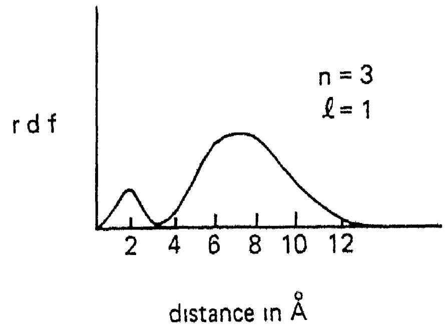
A-104 The Bohr theory would predict that an electron in the n = 2 orbit would be found only at the radius of the second Bohr orbit. Therefore, there would be zero probability of finding the electron at 0.53 Å .

Q-105 According to wave mechanics, would there be any probability of finding a 2s electron in the region of 0.53 Å .

A-105 From Figure II, it can be seen that wave mechanics predicts that there is a probability of finding an electron at a distance of 0.53 Å .

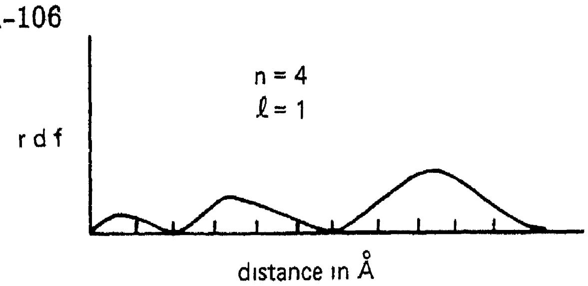
Q-106 The following graphs give the r.d.f. as a function of distance from the nucleus for n = 2, ℓ = 1 (2p orbital) and n = 3, ℓ = 1 (3p orbital).





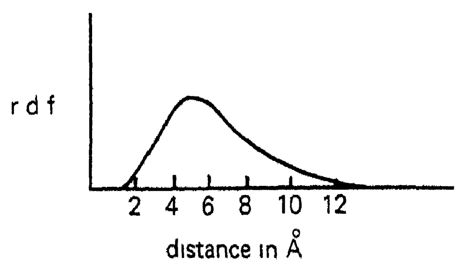
Sketch a diagram to illustrate the r.d f. as a function of distance from the nucleus for an orbital with n = 4, ℓ = 1 (4p orbital). (Hint The number of maxima in the curve will be n-ℓ)

A-106



Q-107 Sketch a diagram to illustrate the r.d f. as a function of distance from the nucleus for an orbital with n = 3, ℓ = 2 (3d orbital)

A-107



R The radial distribution function (r.d.f.) gives the probability of finding an electron a certain distance from the nucleus. The r.d.f. diagrams are dependent upon values of n and ℓ.

S-21 A fourth quantum number, designated as s, is related to the spin of an electron and is called the spin quantum number. The spin of an electron is quantized and may have a value of $+\frac{1}{2}$ or $-\frac{1}{2}$. Each orbital may contain a maximum of two electrons, one with $s = +\frac{1}{2}$ and one with $s = -\frac{1}{2}$ The Pauli exclusion principle states that no two electrons in a given atom can have the same four quantum numbers (n, ℓ, m, and s).

Q-108 According to the Pauli exclusion principle, how many electrons are allowed per orbital?

A-108 Since for a given orbital three quantum numbers would be the same, the fourth quantum number, s, must be different. It can only have the values of $+\frac{1}{2}$ and $-\frac{1}{2}$, therefore, there can be only two electrons per orbital

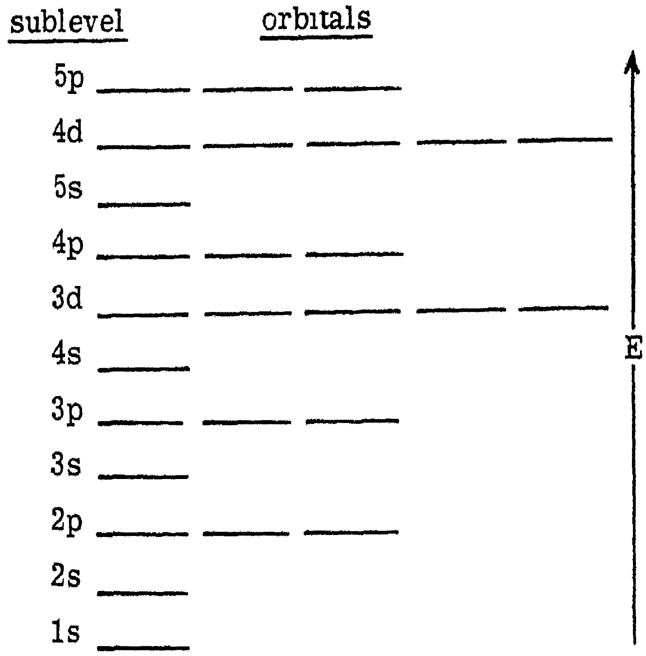
Q-109 How many 2p electrons can have the spin quantum number $+\frac{1}{2}$?

A-109 Since there are three 2p orbitals and each one can contain one electron with $s = +\frac{1}{2}$, the answer is three.	Q-110 How many 3d electrons can have the s quantum number $-\frac{1}{2}$?
A-110 Five.	Q-111 How many electrons can have an ℓ quantum number of 1 and an n quantum number of 2?
A-111 Six.	R a) **Each orbital can contain two electrons. The electron can have a spin quantum number, s, of $\pm\frac{1}{2}$.** b) **No two electrons in an atom can have the same four quantum numbers.**

S-22 Using the concepts of electronic levels and sublevels presented above, the electronic structure of the elements can be built up in terms of filling these levels with electrons. A shorthand notation will be used for writing electronic structures. Earlier the notation 2p was given to represent a p sublevel in the n = 2 energy level. A superscript will now be added to designate the number of electrons in a sublevel. Thus, $2p^4$ represents 4 electrons in the p sublevel of the second energy level.

	Q-112 Write the shorthand notation to illustrate five electrons in the d sublevel of the n = 3 energy level.
A-112 $3d^5$	Q-113 Write the shorthand notation to illustrate 7 electrons in the f sublevel of the n = 4 energy level.
A-113 $4f^7$	Q-114 Interpret the notation $3s^2$.
A-114 This notation means there are two electrons in the s sublevel of the n = 3 energy level.	Q-115 Interpret the notation $2p^1$.
A-115 This notation means there is one electron in a p sublevel in the n = 2 energy level.	Q-116 Interpret the notation $4d^{10}$.
A-116 This notation means there are 10 electrons in the d sublevel of the n = 4 energy level.	

S-23 In building up the electronic configuration of an atom (called the Aufbau process), electrons are added first to orbitals in sublevels of lowest energy. The following diagram shows the relative energy of the sublevels. (The orbitals within each sublevel are also indicated.)



Q-117 Considering the diagram in S-23 and the fact that each orbital will hold only two electrons, show which orbitals would fill first if three electrons were added to the empty sublevels

A-117 two electrons in the 1s
one electron in the 2s

Q-118 Show which orbitals would fill first if 5 electrons were added.

A-118 two electrons in the 1s
two electrons in the 2s
one electron in the 2p

Q-119 If 4 electrons were added to the empty sublevels, how many orbitals would be half-filled?

A-119 two electrons in the 1s
two electrons in the 2s

Therefore, there would be no half-filled orbitals.

Q-120 Would a spectral line be seen for a $3p \rightarrow 2p$ transition?

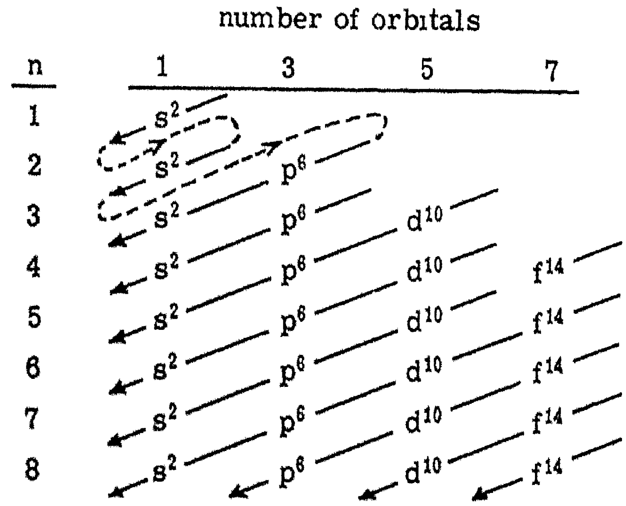
A-120 Yes. Energy would be released in the form of a wave of light when the electron drops from a higher energy level to a lower energy level

Q-121 Would a spectral line be seen for a $2p_x \rightarrow 2p_y$ transition?

A-121 No All the 2p orbitals are of equal energy, therefore, no energy is released in going from one 2p orbital to another 2p orbital.

[redacted]

S-24 Instead of memorizing the energy diagram, a handy memory device can be used for remembering the order in which the orbitals fill.



Q-122 Using the notation given earlier, show the sublevel and the number of electrons in each sublevel for an atom containing 18 electrons. ($1s^2$, $2s^2$, $2p^6$, etc)

A-122 $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$

Q-123 Show the sublevel and the number of electrons in each sublevel for an atom containing 30 electrons.

A-123 $1s^2$, $2s^2$, $2p^6$, $3s^2$ $3p^6$, $4s^2$, $3d^{10}$

Q-124 Show the sublevel and the number of electrons in each sublevel for an atom containing 54 electrons.

A-124 $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$

Q-125 Show the sublevel and the number of electrons in each sublevel for an atom containing 70 electrons.

A-125 $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^{14}$

S-25 Because energy is required to pair electrons, no electron pairing occurs until all orbitals in a given sublevel are half-filled. Hund's rule states that when electrons enter a sublevel of fixed n and ℓ values, available orbitals are singly occupied. An example of this rule can be shown by the electronic structure of nitrogen. Seven electrons must be placed in orbitals:

$$1s^2,\ 2s^2,\ 2p_x^1,\ 2p_y^1,\ 2p_z^1$$

No pairing of electrons occurs in the 2p sublevel until each of the three equal energy orbitals contains one electron.

Q-126 Indicate the number of electrons in each of the orbitals of the 2p sublevel of oxygen.

A-126 There are four electrons to be placed in the three 2p orbitals There will be one electron in each of two orbitals and two electrons in the other one.

2p ↑↓ ↑ ↑

Q-127 In the previous question, after one electron was placed in each of the 2p orbitals, the fourth electron was placed in one of the half-filled orbitals Into which 2p orbital should this electron be placed?

A-127 It does not matter All the p orbitals are of equal energy

Q-128 How many electrons are in each of the 3d orbitals of Mn?

A-128 Mn has five 3d electrons Therefore, there is one electron in each orbital

3d ↑ ↑ ↑ ↑ ↑

Q-129 How many unpaired electrons are there in the electronic structure for Co?

A-129 Three Co has seven 3d electrons. Therefore, three 3d orbitals have only one electron in them

↑↓ ↑↓ ↑ ↑ ↑

Q-130 How many unpaired electrons are there in the electronic structure for Sn?

A-130 Two Two 5p orbitals have 1 electron each

Q-131 How many unpaired electrons are there in the electronic structure for W?

A-131 Four Four 5d orbitals have 1 electron each

Q-132 **Write the electronic structure for Be indicating half-filled orbitals, if any.**

A-132 4 electrons $1s^2$, $2s^2$

Q-133 **Write the electronic structure for C indicating half-filled orbitals, if any.**

A-133 6 electrons $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$

Q-134 **Write the electronic structure for V indicating half-filled orbitals, if any.**

A-134 23 electrons: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^1$, $3d^1$, $3d^1$

It is not necessary to distinguish between the d orbitals.

Q-135 **Write the electronic structure for As indicating half-filled orbitals, if any.**

A-135 33 electrons. $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p_x^1$, $4p_y^1$, $4p_z^1$

Q-136 **Write the electronic structure for Hf indicating half-filled orbitals, if any.**

A-136 72 electrons $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^{14}$, $5d^1$, $5d^1$

Q-137 **Write the electronic structure for potassium, K, with one electron removed (K^+ ion) indicating half-filled orbitals, if any. (Hint: The electron in the outermost orbital is removed in forming the ion.)**

A-137 18 electrons $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$

Q-138 Write the electronic structure for Al^{+3} indicating half-filled orbitals, if any

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A-138 10 electrons $1s^2$, $2s^2$, $2p^6$

Q-139 Write the electronic structure for Br^- indicating half-filled orbitals, if any

---

A-139 36 electrons $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$

Q-140 Write the electronic structure for O^{-2} indicating half-filled orbitals, if any.

A-140 10 electrons $1s^2$, $2s^2$, $2p^6$

R **When adding electrons to orbitals of the same energy, no electron pairing is shown until all orbitals in a given sub-level are half-filled.**

S-26 An interesting anomaly occurs in the electronic structure of some atoms. Extra stability is gained by structures in which equal energy (degenerate) orbitals are either half-filled or completely filled Thus, if an atom needs only one electron to half fill or completely fill equal energy orbitals, it will transfer an electron from the next lower energy orbital to form the more stable structure

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Q-141 What does the term degenerate orbitals mean?

A-141 Orbitals which have the same energy, such as the three p orbitals.

Q-142 Does oxygen have any occupied degenerate orbitals? If so, which ones are degenerate?

A-142 Yes, the three occupied 2p orbitals are equal in energy, and thus are degenerate

Q-143 Does helium have any occupied degenerate orbitals?

A-143 No. There is only a single s orbital occupied in He.

Q-144 By using the memory device (S-24) for filling electrons into atoms, the following structure is obtained ... , $5s^2$, $4d^4$. Remembering that half-filled orbitals are more stable, what structure would be predicted?

A-144 ... $5s^1$, $4d^1$, $4d^1$, $4d^1$, $4d^1$, $4d^1$

Q-145 Explain the electronic structure of chromium:

$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, $3d^1$, $3d^1$, $3d^1$, $3d^1$, $3d^1$

A-145 An electron is transferred from the 4s orbital to give a structure where all the 3d orbitals are half-filled.

Q-146 If by using the memory device the following structure is obtained ... , $4s^2$, $3d^9$, what is the likely structure for the atom?

A-146 . $4s^1$, $3d^{10}$

Q-147 How can you account for the fact that the arrangement in A-144 is more stable than that in Q-144. (Hint The d orbitals are degenerate)

A-147 Five degenerate d orbitals with the same number of electrons in each gives rise to extra stability Little energy is lost in removing an electron from the s orbital since it is not a degenerate orbital

Q-148 Write the electronic structure for Cu showing half-filled orbitals, if any.

A-148 29 electrons $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, $3d^{10}$

Q-149 Write the electronic structure for Mo showing half-filled orbitals, if any.

A-149 42 electrons $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^1$, $4d^1$, $4d^1$, $4d^1$, $4d^1$, $4d^1$

Q-150 Write the electronic structure for Au, showing half-filled orbitals, if any.

A-150 79 electrons: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $4f^{14}$, $5s^2$, $5p^6$, $5d^{10}$, $6s^1$

[redacted]

PART III: Chemical Periodicity

S-1 It has been found experimentally that elements with the same electronic configuration in their outermost occupied energy level have similar chemical and physical properties. This is known as the chemical periodicity of the elements. It is this phenomenon that forms the basis for the arrangement of the elements on the periodic table.

Q-1 Give the electronic structure for Na, Li, and K. How are the electronic structures similar?

A-1 Li: $1s^2$, $2s^1$

Na $1s^2$, $2s^2$, $2p^6$, $3s^1$

K: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$

All the atoms contain a single electron in their outermost occupied energy level

Q-2 What is similar about the electronic structures of Be, Mg, and Ca?

A-2 All the atoms contain a pair of s electrons in their outermost energy level.

Q-3 Would you expect the following to be similar chemically?

Element A: $1s^2$, $2s^2$, $2p^5$

Element B: $1s^2$, $2s^2$, $3s^2$, $3p^5$

A-3 Yes, the two elements have the same electronic structure in their outermost energy level

Q-4 In the periodic table, P is directly under N and As under P Do these elements have anything in common? What?

A-4 Yes, these elements all have the same electronic structure in their outermost energy level, therefore, they are closely related in their physical and chemical properties.

Q-5 Do the elements Cl, Br, and I have anything in common? If so, what?

A-5 Yes, these elements all have the same electronic structure in their outermost energy level.

[redacted]

S-2 A column (down) of elements in the periodic table is called a group. A row (across) of elements is called a period.

Q-6 Give the symbol for several elements whose physical and chemical properties should be similar to those of S.

A-6 O, Se, Te, Po

Q-7 Give the symbol for several elements whose physical and chemical properties should be similar to those of Ca.

A-7 Be, Mg, Sr, Ba, Ra

Q-8 Are the physical properties of vanadium more closely related to niobium or titanium?

A-8 Niobium (in the same group)

Q-9 For the elements in group IA and IIA of the periodic table, in what kind of orbital will the outer electron be?

A-9 s orbitals. These are called alkali (IA) and alkaline earth (IIA) elements.

Q-10 For the elements in groups IIIA, IVA, VA, VIA, and VIIA of the periodic table, which orbitals are being filled?

A-10 p orbitals. These elements are representative elements and each group is named after the first member in the family (exception: the fluorine family is called the halogen family).

Q-11 To what family does As belong?

A-11 Nitrogen family

Q-12 To what family does Ga belong?

A-12 Boron family

Q-13 To what family does Br belong?

A-13 Halogen family

Q-14 For the elements in groups IB through VIIB, including VIII, which orbitals are incompletely filled or just filled

A-14 d orbitals The elements in this section of the periodic table are called transition metals Here again the family name is the same as the first member of the group

Q-15 Elements with all orbitals completely filled in their outer energy level are called inert gases. Give several examples of elements in this family.

A-15 He, Ne, Ar, Kr, Xe, Rn

Q-16 Elements 58 through 71 and 90 through 103 are called inner transition elements. Which orbitals are incompletely filled or just filled in these elements?

A-16 f orbitals

Q-17 The two outside energy levels of an atom have the electronic structure,

$$s^2p^6,\ s^2 .$$

To what family does the atom belong?

A-17 Alkaline earth.

Q-18 The two outside energy levels of an atom have the electronic structure,

$$s^2p^6,\ s^2p^3 .$$

To what family does the atom belong?

A-18 It is a representative element of the nitrogen family.

Q-19 The two outside energy levels of an atom have the electronic structure,

$$s^2p^6d^{10},\ s^2p^6 .$$

To what family does the atom belong?

A-19 Inert gas.

Q-20 The two outside energy levels of an atom have the electronic structure,

$$s^2p^6d^5,\ s^2 .$$

To what family does the atom belong?

A-20 Transition element, manganese family.

Q-21 Identify the family for each of the following elements. The electronic structure of the two outside energy levels is given.

a) $s^2p^6,\ s^1$

b) $s^2p^6d^7,\ s^2$

c) $s^2p^6d^{10}f^{14},\ s^2p^5$

A-21 a) alkali
b) cobalt (transition element)
c) halogen

R The periodic table of elements is classified into groups of elements called alkali, alkaline earth, transition, representative, inner transition, and inert gases. The classification depends on the electronic structure of the outermost energy levels.

S-3 Within a period or group of the periodic table, well defined trends in properties are evident. One property showing a trend is atomic radii which is a measure of the size of the atom.

Q-22 What change is observed in the electronic structure of the outermost energy level of an element in moving down a given group of elements?

A-22 The outer electrons are in an energy level with a higher value of n

Q-23 As n increases how does the size of the charge cloud change?

A-23 Increases.

Q-24 What will determine the size of an atom?

A-24 The size of the charge cloud of its outer electrons.

Q-25 It has been observed experimentally that within each group the atomic radius increases with increasing atomic number. Give the reason for this.

A-25 The increase in size going down a group in the periodic table is the result of adding electrons to energy levels with larger values for n which results in a larger radius for the electron cloud.

Q-26 What generalization can be made concerning the energy level occupied by the outermost electrons of all elements within the same period?

A-26 All outermost electrons are in the same energy level (same value for n).

Q-27 Which element has the larger atomic radius, Na or K?

A-27 K

Q-28 Are there any attractive forces between the nucleus of an atom and the outermost electrons? If so, what is the cause of these attractive forces?

A-28 Yes, there are electrostatic attractive forces between the protons in the nucleus(+) and the electrons(-) in the outermost energy level. The forces are directly proportional to the number of protons in the nucleus.

Q-29 Will these attractive forces increase or decrease as the atomic number increases? Why?

A-29 The attractive forces will increase because the number of protons in the nucleus increases. The attractive forces are directly proportional to the number of protons in the nucleus.

Q-30 Within each period, it has been found that the atomic radius decreases with increasing atomic number. Give the reason for this.

A-30 There is a higher positive charge in the nucleus with increasing atomic number Within a period, the outermost electrons are in the same energy level. The greater attraction between the positive nucleus and the negative electrons tends to contract the size of the electron cloud giving rise to a smaller atom

Q-31 Which element has the larger atomic radius, O or N?

A-31 N

Q-32 Arrange the following set of atoms in order of increasing atomic radius Na, Rb, K, Mg

A-32 Mg (smallest), Na, K, Rb (largest)

Q-33 Arrange the following set of atoms in order of increasing atomic radius. Na, Si, Al, Ar

A-33 Ar, Si, Al, Na

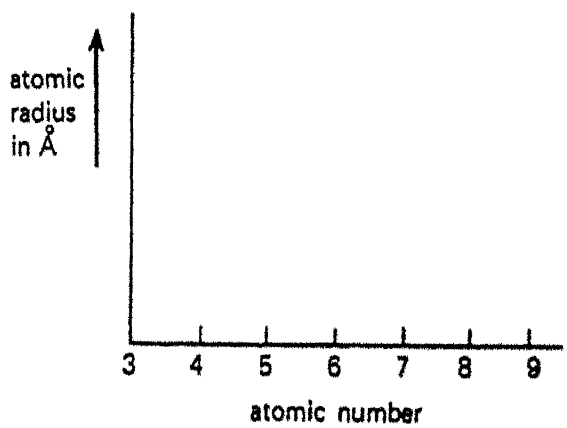
Q-34 Arrange the following set of atoms in order of increasing atomic radius: Mg, Ge, Si, Ca, Sn.

A-34 Si, Mg, Ge, Ca, Sn
(The decrease in size of atomic radius in going from left to right across a period is not as large as the increase in atomic radius caused by the addition of electrons to higher energy levels.)

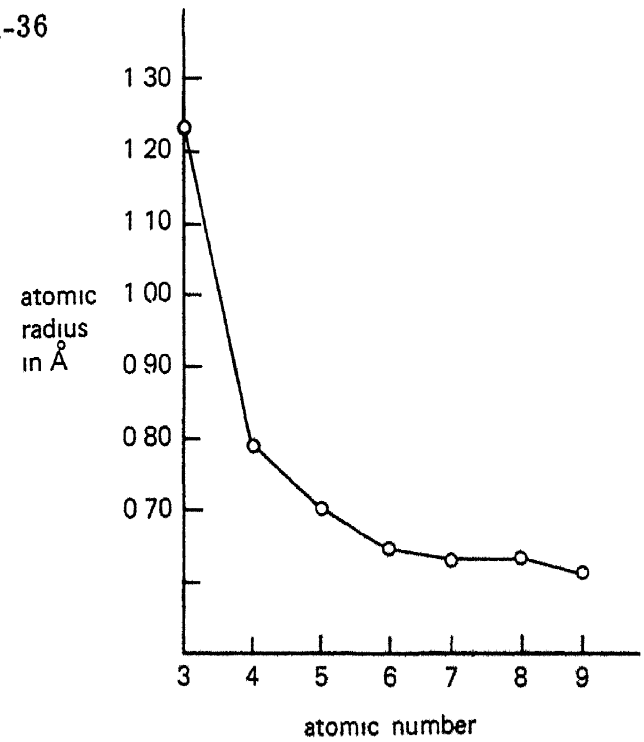
Q-35 Arrange the following set of atoms in order of increasing atomic radius: F, Br, Cl, C, O.

A-35 F, O, C, Cl, Br

Q-36 The electrostatic effect which causes the atom to become smaller in moving across a period diminishes in magnitude in moving from left to right. Sketch a graph which would correctly show the relationship between atomic radii and atomic number for elements in the second period. (The approximate trend is all that is necessary.)

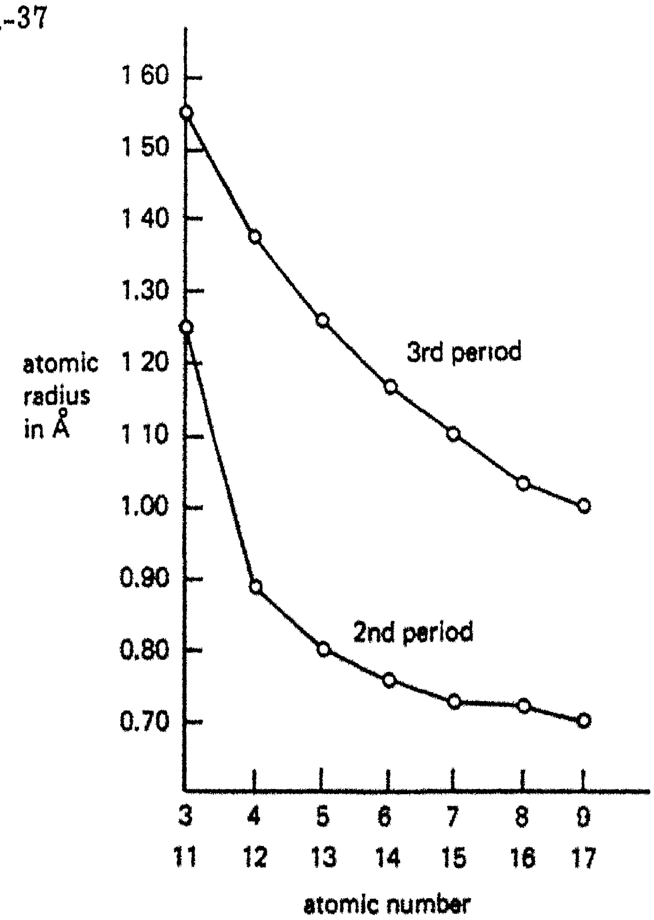


A-36



Q-37 Sketch a graph showing the relationship between atomic radius and atomic number for the second and third periods of elements

A-37

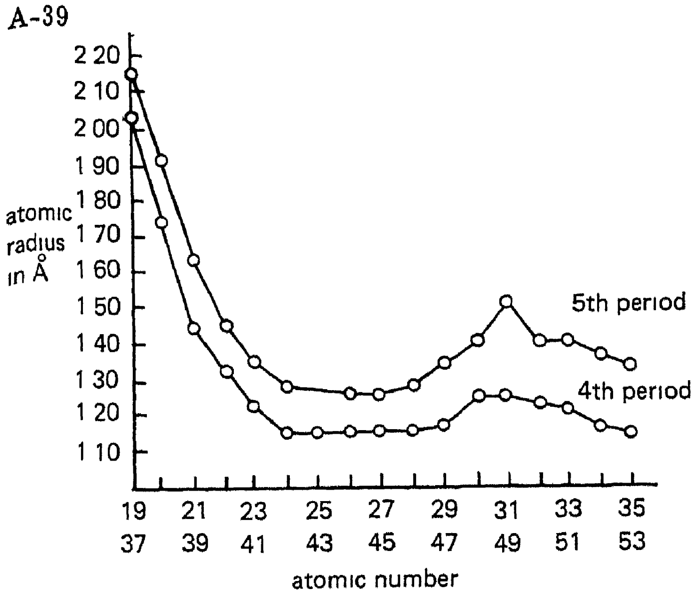


Q-38 The fourth period of the periodic table contains transition elements. What change would be expected in the atomic radius in moving from Sc to Zn?

A-38 A decrease which would grow smaller as Zn is approached. Actually, very little change is observed from Cr through Cu with a slight increase for Zn.

Q-39 Sketch a graph showing the relationship between atomic radius and atomic number for the fourth and fifth periods of elements.

A-39



Q-40 Arrange the following set of atoms in order of increasing atomic radius: Ca, Fe, Br, V.

A-40 Br, Fe, V, Ca

Q-41 Arrange the following set of atoms in order of increasing atomic radius: Sr, V, Nb, Cd, Pd.

A-41 V, Pd, Cd, Nb, Sr

Remember, there is a small increase in atomic radius at the end of each transition period.

Q-42 The radii of Zr (5th period) and Hf (6th period) are nearly equal. Offer an explanation. (Hint: Hf has fourteen 4f electrons.)

A-42 The addition of electrons to the 4f level adds no new energy levels to the atom. The addition of protons to the nucleus causes a large attraction between the nucleus and the electrons. This produces a contraction in the size of the electron shell The contraction in the size of the Hf atom because of the 14 protons just offsets the increase in size due to the additional electronic energy level.

Q-43 Would the atomic radius of Mo be expected to be closer to the radius of W or Cr?

A-43 Closer to W. (See A-42)

Q-44 Which two of the three elements Au, Cu, and Ag would be expected to have nearly the same atomic radius.

A-44 Au and Ag. (See A-42)

[redacted]

S-4 Ionization energy is defined as the energy needed to remove an electron from the outermost occupied energy level of an atom.

Q-45 Write the reaction which the ionization potential of Li measures.

A-45 $Li_{(g)} \rightarrow Li^{+}_{(g)} + e^{-}$

Q-46 It has been determined that within a given group the ionization energy decreases with increasing atomic number Give a reason for this observation

A-46 As the atomic number increases, the outermost electrons are in energy levels of increasingly higher energy These higher energy level electrons are further from the nucleus and are partially shielded from the nuclear attraction by inner electrons. Therefore, the additional energy necessary to cause ionization is less.

Q-47 It has been observed that the ionization energy increases with increasing atomic number within a given period Explain

A-47 In small atoms, the outer electrons are closer to the positive nucleus and are more tightly held than in large atoms where the outer electrons are further from the nucleus

Q-48 Which element has the higher ionization energy, Na or K?

A-48 Na

Q-49 Which element has the lower ionization energy, F or I?

A-49 I

Q-50 Which element has the higher ionization energy, N or C?

A-50 N

Q-51 Within a given period, there are always some atoms whose ionization energy appears to be out of line. In the second period there are two regressions, one after Be and the other after N. This is because each of these two atoms has an "abnormally" large ionization energy. Write out the electronic configurations for Li, Be, B, C, and N.

A-51 Li: $1s^2$, $2s^1$

Be: $1s^2$, $2s^2$

B: $1s^2$, $2s^2$, $2p^1$

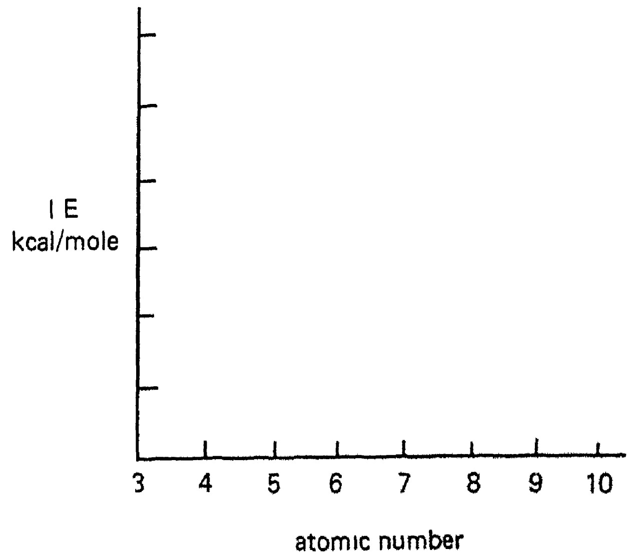
C: $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$

N: $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$

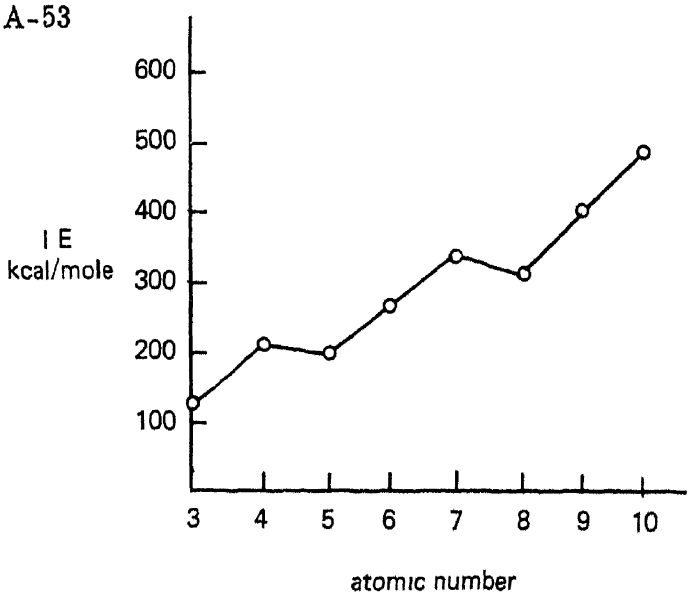
Q-52 Is there anything about the electronic configuration of Be and N which might explain their high ionization energy?

A-52 The electron removed from Be is from a filled 2s orbital The electron removed from N is from a configuration where each 2p orbital is half-filled More energy is required to remove an electron from a configuration where all orbitals are either half-filled or completely filled due to the extra stability of these configurations

Q-53 Draw a graph showing the relationship between ionization energy and atomic number for the second period elements



A-53

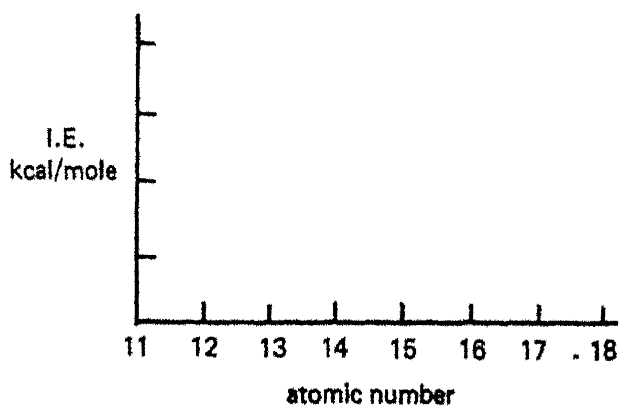


Q-54 Which elements in the third period would be expected to have "abnormally high" I. E. ? Why?

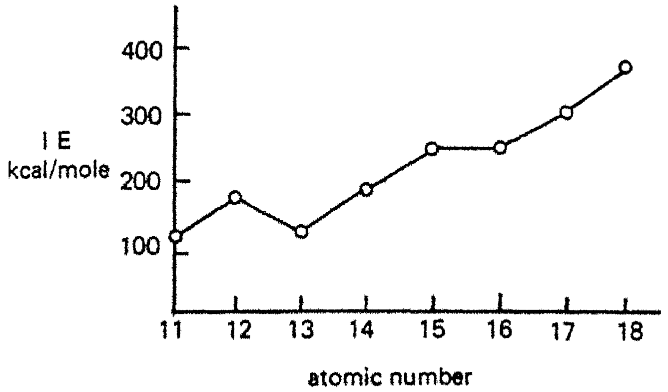
A-54 Mg, P, and Ar

These elements have filled or half-filled orbitals. These three elements do, in fact, have I E. higher than might be expected.

Q-55 Draw a graph showing the relationship between I. E. and atomic number for the third period elements.



A-55



Q-56 Would the first ionization energy of Co be expected to be greater or less than the ionization energy of Sc? Why?

A-56 Co is a smaller atom and has a higher nuclear charge than Sc; therefore, the attractive forces in Co are larger and the ionization energy larger.

Q-57 Arrange the following set of atoms in order of increasing ionization energy: Zn, Ga, K.

A-57 K, Ga, Zn

Q-58 In the previous question, account for the fact that the ionization energy for Ga is lower than that for Zn.

A-58 The electron removed from Ga is a 4p electron. The electron removed from Zn is from a filled 4s orbital. The 4p electron is at a higher energy and is less tightly held by the nucleus than a 4s electron. Thus, it is more easily removed.

Q-59 Arrange the following set of atoms in order of increasing ionization energy: Se, As, Ge.

A-59 Ge, Se, As

As is "abnormally" high because an electron must be removed from half filled degenerate orbitals.

Q-60 Arrange the following set of atoms in order of increasing ionization energy: Na, P, Si, Al, S.

A-60 Na, Al, Si, S, P

Q-61 Arrange the following atoms in order of increasing ionization energy: K, Cs, Rb, Ca.

A-61 Cs, Rb, K, Ca

Q-62 Arrange the following set of atoms in order of increasing ionization energy: Br, Se, Ge, As.

A-62 Ge, Se, As, Br.

Q-63 Arrange the following atoms in order of increasing ionization energy: W, Cr, Fe, Cs.

A-63 Cs, W, Cr, Fe

[redacted]

S-5 In the formation of ions from the neutral atom, electrons are lost from the outermost occupied energy level.

Q-64 Consider the ion Li^+ Would the radius of this ion be expected to be a) greater than, b) less than, or c) the same as the radius of a neutral Li atom? Why?

A-64 The outermost electrons in the Li^+ ion are in the n = 1 energy level while the outermost electrons in the Li atom are in the n = 2 energy level. Since the outermost electrons determine the radius, the Li^+ ion would be expected to have a smaller radius.

Q-65 Which ion would be expected to have the smaller radius Li^+ or Be^{+2}? Why?

A-65 Be^{+2}. The outermost electrons in both ions are in the n = 1 energy level However, the Be^{+2} nucleus has 4 protons, while the Li^+ nucleus has only 3 protons Therefore, the electrostatic attraction between the Be^{+2} nucleus and the outermost electrons will be greater

Q-66 Even though the outermost electrons in the fluoride ion (F^-) are all in the n = 2 energy level, the fluoride ion has a much larger radius than the fluorine atom. Offer an explanation. (Hint. Do electrons attract each other?)

A-66 The outermost electrons in an atom repel each other This repulsion is counterbalanced by the attraction to the nucleus By adding another electron to the outermost energy level of electrons (to form F^-), the electrostatic repulsion of the electrons has been increased and the electrostatic attraction between the nucleus and the outermost electrons has <u>not</u> been increased.

Q-67 Which of the ionic species would be expected to have the greater radius, O^- or O^{-2}? Why?

A-67 In both O^- and O^{-2}, the outermost electrons are in the n = 2 energy level and the nuclei contain the same number of protons Since the electrostatic repulsion between electrons in O^{-2} would be greater than in O^-, O^{-2} would be expected to have the greater radius.

Q-68 Which of the two species would be expected to have the greater radius, the O^- ion or F atom? Why?

A-68 As stated previously, the F^- ion is much larger than F atom. Therefore, it is expected that the O^- ion would be larger than O atom. Since O atom is larger than F, the O^- ion must be larger than F.

Q-69 The O^{-2} ion has a greater radius than F^-. Would N^{-3} be expected to have a radius greater than, equal to, or less than O^{-2}?

A-69 Greater than O^{-2}.

Q-70 Which ion would be expected to be larger, Be^{+2} or B^{+3}?

A-70 Be^{+2} should be larger because the 5 protons in the nucleus of B^{+3} would exert a greater electrostatic effect than the 4 protons in Be^{+2}

Q-71 What general statement could be made about the radius of positive and negative ions and their neutral atoms?

A-71 A positive ion will always be smaller than the neutral atom and the negative ion will always be larger than the neutral atom.

$M^- > M > M^+$

Q-72 Which species would be expected to have the larger radius, Co^{-2} or Fe? Why?

A-72 Fe has the larger radius. The outermost electrons of Co^{+2} are the 3d electrons while the outermost electrons in Fe are 4s electrons.

R

a) In the formation of an ion, electrons are lost from the outermost energy level.

b) The size of ions decreases in the following order:

$$M^- > M > M^+$$

S-6 A group of ions or atoms of different elements which have the same number of electrons are considered to be <u>isoelectronic</u>. For example, I^-, Xe, and Cs^+ are all isoelectronic.

Q-73 Which two ions (or atoms) of the following are isoelectronic with one another.

Na^+, K^+, Ne, O ?

A-73 Na^+ and Ne.

Q-74 Give an example of a positive ion and a negative ion that is isoelectronic with argon.

A-74 K^+ and Cl^- or Ca^{+2} and S^{-2}.

Q-75 Give an example of a positive ion and a negative ion that is isoelectronic with F^-.

A-75 O^{-2} and Mg^{+2} or Na^+.

Q-76 Which isoelectronic species would be expected to have the larger radius, C^{-4} or Ne? Why?

A-76 C^{-4}. It has fewer protons in the nucleus (6) than Ne(10).

Q-77 Arrange the isoelectronic species C^{-4}, N^{-3}, O^{-2}, F^-, and Ne in order of increasing size. Explain why this order was selected.

A-77 $Ne < F^- < O^{-2} < N^{-3} < C^{-4}$ largest

This order was selected because the number of protons increases from C to Ne while the electronic structure remains the same in all species.

Q-78 Is Na^+ isoelectronic with Li^+? Why?

A-78 No. Isoelectronic means that the two species have the same number of electrons Na^+ has 10 electrons while Li^+ has only 2 electrons

Q-79 Which of the following would be expected to be larger S^{-2} or O^{-2}? Why?

A-79 S^{-2} would be larger because the electrons are in the $n=3$ energy level

Q-80 Which of the following would be expected to be smaller, Al^{+3} or Mg^{+2}? Why?

A-80 Al^{+3} and Mg^{+2} and Ne are isoelectronic Since Al^{+3} has a higher nuclear charge, Al^{+3} should be smaller than Mg^{+2}

Q-81 Arrange the isoelectronic species O^{-2}, Ne and Mg^{+2} in order of increasing size. Give the reason for selecting this order

A-81 $Mg^{+2} < Ne < O^{-2}$

This order was selected because the number of protons increase from O^{-2} to Mg^{+2} while the energy levels are the same

Q-82 Arrange the isoelectronic species P^{-3}, S^{-2}, Ar, Ca^{+2} and Ti^{+4} in order of increasing size. Give the reason for selecting this order.

A-82 $Ti^{+4} < Ca^{+2} < Ar < S^{-2} < P^{-3}$

This order was selected because the electronic structure remains the same but the number of protons increase from P^{-3} to Ti^{+4}.

[redacted]

S-7 A spinning charge gives rise to a magnetic field. Electrons (spinning charges) with spin quantum numbers of $+\frac{1}{2}$ and $-\frac{1}{2}$ give rise to magnetic fields oriented in opposite directions. An atom that contains unpaired electrons (orbitals containing one electron) is attracted to a magnetic field and is said to be paramagnetic. In an atom that contains only paired electrons, the magnetic fields caused by the electron spin cancel each other. Atoms that contain only paired electrons are repelled by a magnetic field and are said to be diamagnetic.

Q-83 **Which of the following atoms would be paramagnetic: Be, Ca, N, Zn?**

A-83 N

Q-84 **Which of the following atoms would be paramagnetic: O, Al, K, Ne?**

A-84 O, Al, and K

Q-85 **Which of the following atoms would be paramagnetic: Cd, Sn, Ba, Co?**

A-85 Sn and Co

Q-86 **Which atom would be attracted to a magnetic field, Sr or Mo?**

A-86 Mo

Q-87 **Which atom would be repelled by a magnetic field, Pb or Hg?**

A-87 Hg

Chapter 4 | *CHEMICAL BONDING*

Part I: Lewis Electronic Formulas

After completing this section you should be able to

a) write Lewis electronic dot formulas for ionic and covalent compounds
b) understand forces between atoms in an ionic bond.

Part II: Valence Bond Theory

After completing this section you should be able to

a) understand interactions present in a covalent bond
b) write the valence bond description for bonding in covalent molecules
c) illustrate the orbital overlap for bonding in covalent molecules.

Part III: Hybridization

After completing this section you should be able to

a) predict bond angles from a knowledge of the hybridization of atoms
b) predict hybridization from a knowledge of bond angles in molecules.

Part IV: Repulsion Theory

After completing this section you should be able to

a) predict the geometry of molecules.

Part V: Electronegativity

After completing this section you should be able to

a) predict if atoms will form ionic or covalent bonds
b) understand dipole moments of molecules and bond energies.

Part VI: Resonance

After completing this section you should be able to

a) write resonance structures for molecules.

Part VII: Hydrogen Bonding

After completing this section you should be able to

a) understand when hydrogen bonding occurs and the results of these interactions.

PART I: Lewis Electronic Formulas

S-1 In studying the combination of atoms to form molecules, only the valence electrons of an atom will be of concern The valence electrons are usually the electrons in the outermost occupied energy level (valence shell) of each atom Initially, only electrons in the valence shell will be considered.

	Q-1 How many valence electrons does hydrogen have?
A-1 1 electron	Q-2 How many valence electrons does carbon have? Which electrons are they?
A-2 4 valence electrons $2s^2$ $2p^2$	Q-3 How many valence electrons does oxygen have? Which electrons are they?
A-3 6 valence electrons $2s^2$ $2p^4$	Q-4 How many valence electrons does chlorine have? Which electrons are they?
A-4 7 valence electrons $3s^2$ $3p^5$	Q-5 What is the maximum number of valence electrons possible for atoms in the second period of the periodic table (Li → Ne)?
A-5 There is a possibility of two s electrons and six p electrons making a total of 8 possible valence electrons.	R Valence electrons are [illegible] the electrons in the [illegible] ergy level (valence shell) [illegible]

S-2 A new type of symbol will be employed to represent the number and arrangement of the valence electrons. This representation places dots around the symbol of the atom. For example, nitrogen is represented in the following manner·

$$\cdot\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot$$

The two dots on top represent two electrons in the s orbital and the other three dots represent one electron in each p orbital.

	Q-6 Write the electron dot symbol for Be.
A-6 $\overset{\cdot\cdot}{Be}$ two s electrons	Q-7 Write the electron dot symbol for oxygen showing two unpaired electrons.
A-7 $.\overset{\cdot\cdot}{\underset{\cdot}{O}}\cdot$ two s electrons and four p electrons	Q-8 Write the electron dot symbol for fluorine.
A-8 $:\overset{\cdot\cdot}{\underset{\cdot}{F}}\cdot$ two s electrons and five p electrons	Q-9 Write the electron dot symbol for neon.

A-9 $\underset{\cdot\,\cdot}{\text{Ne}}\ \cdot$

Q-10 Consider the electron dot symbol for Li, Na, K, and Rb What conclusion can be made about electron dot symbols for elements within the same family?

A-10 $\dot{\text{Li}}$, $\dot{\text{Na}}$, $\dot{\text{K}}$, $\dot{\text{Rb}}$

The electron dot symbols are all the same, since each element has the identical number of valence electrons

R **The electron dot symbol is used for showing the number of valence electrons around an atom.**

S-3 There are two basic types of chemical bonds, <u>electrostatic</u> and <u>covalent</u>. They can be distinguished by their electrical properties Compounds which are made up of atoms held together by electrostatic bonds (ionic compounds) conduct electricity in solution or in the molten state Compounds which are made up of atoms held together by covalent bonds (nonionic compounds) do not conduct electricity. In the formation of an electrostatic bond between two atoms, a valence electron is transferred from the atom with the greater tendency to lose electrons to the atom with a greater affinity for the electron. The bond is due to the coulombic forces between the oppositely charged ions. Most chemical bonds are neither purely electrostatic nor purely covalent but have varying degrees of ionic character.

Q-11 Sodium and chlorine form an ionic compound sodium chloride, NaCl. Sodium loses one electron while chlorine gains an electron. Write the electron dot symbols for sodium and chlorine in this compound, NaCl. A positive charge (+) should be indicated on the atom which lost an electron and a negative charge (-) should be indicated on the atom which gained an electron.

A-11 Na^+ $\quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^-$

Sodium has a charge of +1 since it has lost one electron. Chlorine has a charge of -1 since it has gained one electron.

Q-12 A general rule for atoms forming ionic compounds is that the atom farthest to the left in the periodic table loses electrons and the atom farthest to the right gains electrons. In the ionic compounds below, which atom gains electrons and which loses electrons?

a) KBr b) LiF

A-12 a) K loses Br gains

b) Li loses F gains

Q-13 In the ionic compounds below, which atom gains electrons and which loses electrons?

a) CaI_2 b) MgO c) Rb_2S

A-13 a) Ca loses I gains

b) Mg loses O gains

c) Rb loses S gains

Q-14 From the two preceding questions, what generality can be made concerning the order of writing the symbols for elements in the formula of an ionic compound?

A-14 The positive ion is written first For example, the formula for a salt containing potassium (K) and bromine (Br) is KBr K is the positive ion and Br is the negative ion

Q-15 In general, the number of electrons gained or lost by an atom forming an electrostatic bond is equal to the number of electrons needed to vacate the valence shell or the number of electrons needed to completely fill the valence shell. Give the number of electrons gained or lost by each atom in the following ionic compounds.

a) CsBr b) BaO

A-15 a) Cs one lost
Br one gained

b) Ba two lost
O two gained

Q-16 Give the number of electrons gained or lost by the atoms in each of the following ionic compounds

a) LiI b) SrS

A-16 a) Li loses 1 I gains 1

b) Sr loses 2 S gains 2

Q-17 Give the number of electrons gained or lost by the atoms in the following ionic compounds:

a) CaF_2 b) $MgCl_2$

A-17 a) Ca loses 2 F gains 1

b) Mg loses 2 Cl gains 1

Q-18 In the last examples of ionic compounds, why were the formulas for calcium fluoride and magnesium chloride written as CaF_2 and $MgCl_2$ instead of CaF and MgCl?

A-18 Since Ca and Mg atoms lose two electrons and Cl and F atoms can gain only one electron, two atoms each of Cl and F are necessary to accept the two electrons lost from the Ca or Mg

Q-19 RbBr is an ionic compound. Write an electron dot symbol (Lewis formula) to illustrate the bonding in this compound.

A-19 Rb^+ $\cdot\underset{\cdot\cdot}{Br}\cdot^-$

Q-20 Write an electron dot symbol (Lewis formula) to illustrate the electrostatic bonding in BaS and SrO.

A-20

Ba^{+2} $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}\cdot^{-2}$

Sr^{+2} $\cdot\underset{\cdot\cdot}{O}\cdot^{-2}$

Q-21 Write Lewis formulas to illustrate the electrostatic bonding in $CaBr_2$ and K_2S.

A-21

$\cdot\overset{\cdot\cdot}{\underset{\cdot}{Br}}\cdot^-$ Ca^{+2} $\cdot\overset{\cdot\cdot}{\underset{\cdot}{Br}}:^-$

K^+ $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:^{-2}$ K^+

Q-22 Write Lewis formulas to illustrate the electrostatic bonding in CsF, $InCl_3$, and Rb_3N.

A-22

Cs^+ $\ddot{F}\cdot^-$

$\cdot\dot{Cl}^-$ In^{+3} $.Cl^-$

$:\ddot{Cl}.^-$

Rb^+ $\cdot\ddot{N}^{-3}$ Rb^+

Rb^+

R. The two basic types of chemical bonds are electrostatic and covalent. Most chemical bonds are neither purely electrostatic nor purely covalent. An electrostatic bond is formed when a valence electron is transferred from the atom with the greater tendency to lose electrons to the atom with a greater affinity for electrons.

S-4 In the formation of a covalent bond between two atoms, valence electrons of these atoms are <u>shared</u>. When two electrons are shared between two atoms, a single covalent bond is formed. The sharing of electrons usually allows both atoms to fill their valence shells. To represent the way the valence electrons are distributed in a molecule, electron dot symbols (Lewis formulas) will be used. Examples are

H_2O $\quad$ H
x·
H x O :
··

OF_2 $\quad$ xx ·· xx
x F x O x F x
xx ·· xx

Note that a filled valence shell for H contains only two electrons while filled valence shells for second row elements contain eight electrons. Since most atoms achieve a filled valence shell with eight electrons, a statement of this fact is generalized by the octet rule (atoms combine so that each atom is surrounded by an octet (8) of electrons). The crosses and dots represent the valence electrons of different atoms. No difference actually exists between electrons from different atoms. In writing a Lewis formula, add the number of valence electrons for each atom in the molecule (add to this one electron for each negative charge if working with an ion) and distribute these electrons so that each atom has eight electrons around it (except hydrogen).

Q-23 Write the Lewis formula for the covalent molecules: H_2 and F_2.

A-23 H x H $\quad$ 2 electrons

:F x F: $\quad$ 14 electrons

Q-24 Write the Lewis formula for the following covalent molecules:

a) Br_2 $\quad$ b) NH_3 (Nitrogen is bonded to three hydrogen atoms.)

A-24 a) : Br x Br x $\quad$ 14 electrons

b) H x N x H $\quad$ 8 electrons
$\quad$ H

Q-25 It is customary to use a line to represent a pair of electrons shared between two atoms. Using this notation, write Lewis formulas for the following covalent compounds:

a) HF $\quad$ b) CH_4 (Carbon is bonded to four hydrogen atoms.)

A-25

a) $H \times F \cdot$ $\quad$ $H-F\cdot$ $\quad$ 8 electrons

b)

```
   H          H
   x          |
H x C x H  H—C—H     8 electrons
   x          |
   H          H
```

A dash (—) between atoms represents two electrons shared between these atoms

Q-26 Write Lewis formulas for the following covalent compounds

a) H_2O_2 $\quad$ b) CCl_4 $\quad$ c) H_2S

(In H_2O_2, the oxygen atoms are bonded to each other and to one hydrogen atom In CCl_4, carbon is bonded to four chlorine atoms. In H_2S, sulfur is bonded to two hydrogen atoms

A-26

a) H—O—O—H $\quad$ 14 electrons

b) $\quad$ 32 electrons

```
     . Cl
        |     .
   Cl—C—Cl
   ..   |
       Cl
```

c) $\quad$ 8 electrons

```
  H
  |
 ·S—H
  .
```

R A covalent bond is formed between two atoms when valence electrons of these atoms are shared. A single covalent bond is formed when two electrons are shared between two atoms.

S-5 In some cases, one atom will donate both the electrons involved in bond formation between two atoms. This type of bond is called a <u>coordinate-covalent bond</u> and is sometimes designated by drawing an arrow from the donor to the acceptor atom. For example

$$-B \leftarrow N- \quad \text{or} \quad -B-N-$$

(boron can accept a pair of electrons which nitrogen has available.)

Q-27 Write a Lewis formula for the compound BF_3NH_3 (each F is bonded to the B atom and each H is bonded to the N atom.)

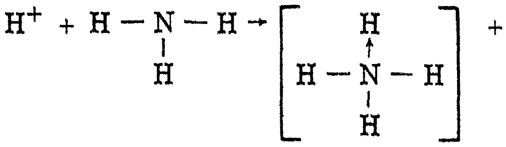
A-27 $\quad$ 32 electrons

```
     .
     F.  H
     |   |
  F—B ← N—H
  .  |   |
    :F:  H

      or
     ..
    ·F: H
 ..  |  |
 ·F—B—N—H
 ..  |  |
    ·F: H
     .
```

Q-28 Write a Lewis formula for the ammonium ion (NH_4^+). Nitrogen is bonded to four hydrogen atoms.

A-28 The NH_4^+ ion is formed from a combination of a hydrogen ion and a neutral ammonia molecule.



8 electrons

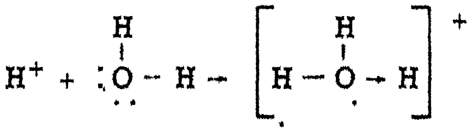
(The bracket is used to indicate that the whole radical is an ion with a positive charge)

Q-29 For the ammonium ion, would it be possible to distinguish the coordinate covalent bond from the other three bonds?

A-29 No, all electrons are identical. Therefore, there would be no way of knowing if the two electrons forming a bond both came from the nitrogen or one each from nitrogen and hydrogen.

Q-30 Write the Lewis formula for the hydronium ion (H_3O^+)

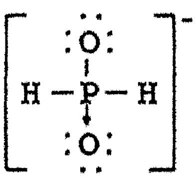
A-30 The H_3O^+ ion is formed from a combination of a hydrogen ion and a neutral water molecule·



8 electrons

Q-31 Write the Lewis formula for the $PH_2O_2^-$ ion Phosphorus is bonded to both hydrogen atoms and both oxygen atoms.

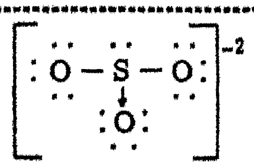
A-31



20 electrons

Q-32 Write the Lewis formula for the sulfite ion (SO_3^{-2}). Sulfur is bonded to three oxygen atoms.

A-32



26 electrons

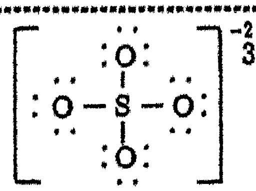
From this point on arrows will no longer be used to designate coordinate-covalent bonds.

Q-33 Write Lewis formulas for the following:

a) SO_4^{-2} sulfate ion, sulfur is bonded to four oxygen atoms

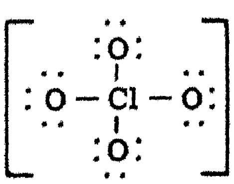
b) ClO_4^- perchlorate ion, chlorine is bonded to four oxygen atoms.

A-33 a) $SO_4^=$



32 electrons

b) ClO_4^-



32 electrons

Q-34 Write the Lewis formula for the chlorate ion, ClO_3^-. Chlorine is bonded to three oxygen atoms.

A-34 $\left[\dot{O} - \underset{\underset{\dot{O}}{|}}{Cl} - \dot{O} \right]^-$ 26 electrons

R When one atom donates both electrons involved in bond formation between two atoms, a coordinate-covalent bond results.

S-6 Some atoms can achieve a full valence shell when more than one electron pair forms a bond between two atoms. This leads to the formation of double and triple covalent bonds The Lewis formula for ethylene, C_2H_2, would be written as

$$\begin{array}{ccccc} & H & & H & \\ & \circ & & \circ\times & \\ H \circ & C & \overset{\times}{\underset{\times}{\times}} & C \overset{\circ}{\underset{\times}{}} & H \end{array} \quad \text{or} \quad \begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H - & C & = & C & - H \end{array}$$

Ethylene has a double bond between the carbons By showing four electrons between the carbon atoms, each carbon atom has eight electrons in its valence shell

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Q-35 Write the Lewis formula for carbon dioxide, CO_2. The carbon is bonded to each oxygen atom

---

A-35 16 electrons·

$O \ \overset{\times}{\underset{\times}{\times}} C \overset{\times}{\underset{\times}{\times}} \ O$ or $\dot{O} = C = O$

Q-36 Write the Lewis formula for CH_2O Carbon is bonded to both hydrogens and the oxygen.

A-36 12 electrons

$$\begin{array}{c} H \overset{\cdot}{\underset{\circ}{}} C \,^\circ H \\ \times\times \\ \overset{\times}{\underset{\times}{}} O \overset{\times}{\underset{\times}{}} \end{array} \quad \text{or} \quad \begin{array}{c} H - C - H \\ \| \\ \overset{\times}{\underset{\times}{}} O \overset{\times}{\underset{\times}{}} \end{array}$$

Q-37 Write the Lewis formula to represent the triple bond in N_2.

A-37 N_2 10 electrons

$\overset{\times}{\underset{\times}{}} N \overset{\times\times\times}{\vdots} N$ or $\overset{\times}{\underset{\times}{}} N \equiv N.$

Q-38 Write the Lewis formula for hydrogen cyanide, HCN In HCN, the carbon atom is bonded to hydrogen and nitrogen.

A-38 HCN 10 electrons

$H \overset{\circ}{\underset{\times}{}} C \overset{\times\times\times}{\vdots} N \colon$ or $H - C \equiv N.$

Q-39 Write the Lewis formula for acetylene, C_2H_2. The carbon atoms are bonded together and each carbon atom has one hydrogen bonded to it.

A-39 $H \overset{\cdot}{\underset{\circ}{}} C \overset{\times\times\times}{} C \overset{\circ}{\underset{\circ}{}} H$ or $H - C \equiv C - H$

(triple bond)

By sharing six electrons between the carbon atoms, each carbon atom can have eight electrons in its valence shell.

Q-40 Write Lewis formulas for the following:

a) NO_3^- nitrate ion. All three oxygen atoms are bonded to nitrogen.

b) N_2O The two nitrogen atoms are bonded together.

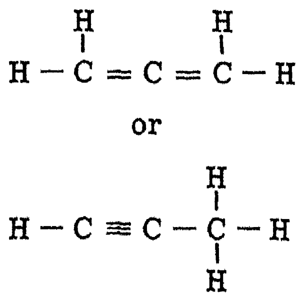
A-40 a) NO_3^- $\left[\begin{array}{c} \dot{O}\colon \\ | \\ O \cdot \overset{\times}{\underset{\times}{}} \underset{\circ}{N} - \ddot{O} \end{array} \right]$ 24 electrons

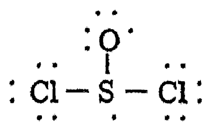
b) N_2O $. \ddot{N} = N = \dot{O}.$ 16 electrons

Q 41 Write the Lewis formula for the following molecules:

a) C_3H_4 The three carbon atoms are bonded together.

b) $SOCl_2$ All atoms are bonded to sulfur.

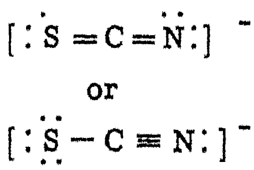
A-41 a)  16 electrons

b)  26 electrons

Q-42 Write Lewis formulas for the following:

a) SCN^- Carbon is bonded to sulfur and nitrogen.

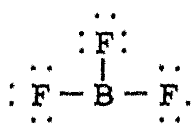
b) O_3

A-42 a)  16 electrons

b)  18 electrons

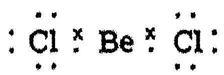
Q-43 Write the Lewis formula for boron trifluoride, BF_3.

Three fluorine atoms are attached to boron by identical bonds. (Boron has only six electrons around it.)

A-43  24 electrons

This is an exception to the octet rule.

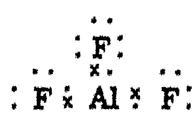
Q-44 Another exception to the octet rule (valence shell of each atom contains 8 electrons) is $BeCl_2$. Write a possible Lewis formula for this molecule Beryllium to chlorine bonds are single bonds.

A-44  16 electrons

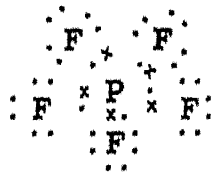
Be has only 4 electrons in its valence shell.

Q-45 Many other atoms do not follow the octet rule, especially those that have inner d orbitals which can accept more electrons. Some other exceptions are AlF_3 (6 electrons around Al), PF_5 (10 electrons around P), and SF_6 (12 electrons around S). Write Lewis formulas for the three exceptions given above.

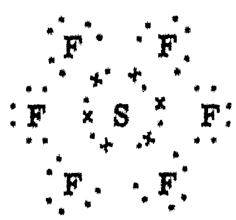
A-45 a) AlF_3 24 electrons



b) PF_5 40 electrons



c) SF_6 48 electrons



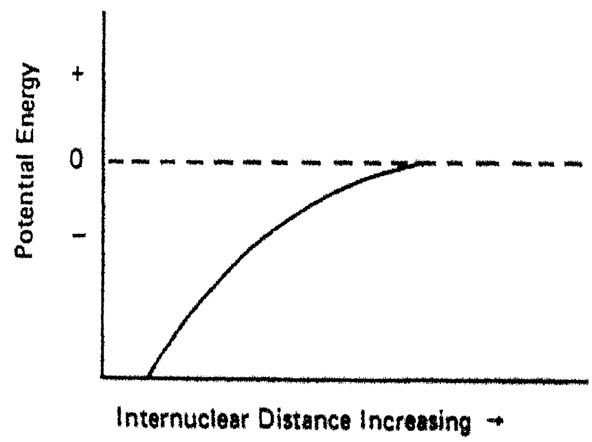
PART II: Valence Bond Theory

S-1 The Lewis formula can be used as a guide for writing structures, but it does nothing to help answer the questions concerning the forces of interaction, the energy of the bond, and the geometry of the molecule For answers to these questions the valence bond theory is useful. According to this theory, bonding occurs by the exchange of electrons between the atoms forming the bond This exchange of electrons is made possible by the overlap of valence electron orbitals of one atom with the valence electron orbitals of another atom Consider two atoms, each with a valence orbital with one electron in it As these atoms are brought together, there is an attractive force which lowers the energy of the system (more stable system) This attractive force is due to the overlap of orbitals permitting the exchange of electrons from one atom to the other The exchange of an electron from one atom to another places two electrons in the same orbital Consequently, the overlap of orbitals is permitted by the Pauli exclusion principle only if the electrons are of opposite spin (different spin quantum number) If the electrons have the same spin, there is a repulsion between the electrons causing no orbital overlap When this occurs, there is no attraction between atoms and thus, there is no bonding

Q-1 Why does the Pauli exclusion principle permit bonding only if the electrons are of different spins?

A-1 With the overlap of orbitals, the two electrons exchange and occupy the same orbital The Pauli exclusion principle states that no two electrons in an atom can have all four quantum numbers the same For the electrons to be in the same orbital, three quantum numbers must be the same, therefore, the spin quantum numbers must be different.

Q-2 The greater the overlap of the orbitals involved in bonding, the stronger is the resulting bond. Below is a plot of potential energy vs internuclear distance for the attractive forces between atoms. Considering only attractive forces, if the overlap of the orbitals increases, how does the potential energy of the system vary?

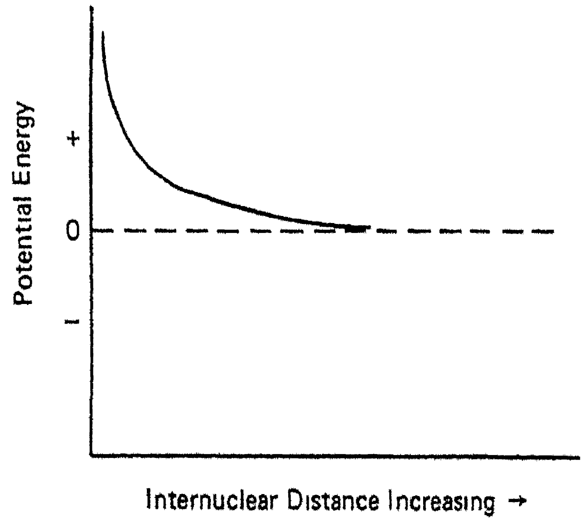


A-2 Considering only attractive forces, if the overlap of the orbitals increases, internuclear distance decreases and the potential energy of the system decreases

Q-3 As the potential energy of a system is lowered, does the strength of the bond increase or decrease?

A-3 As potential energy decreases, the strength of the bond increases (A negative potential energy indicates attraction.)

Q-4 Below is a plot of potential energy vs internuclear distance for the repulsive forces between atoms What gives rise to repulsive forces between atomic nuclei?

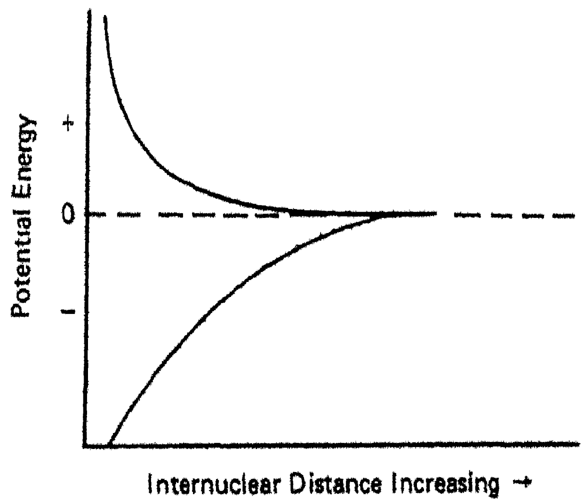


A-4 The two nuclei are positively charged and like charges repel each other (coulombic repulsion).

Q-5 Considering only repulsive forces, if the internuclear distances decreases, does the potential energy of the system increase or decrease.

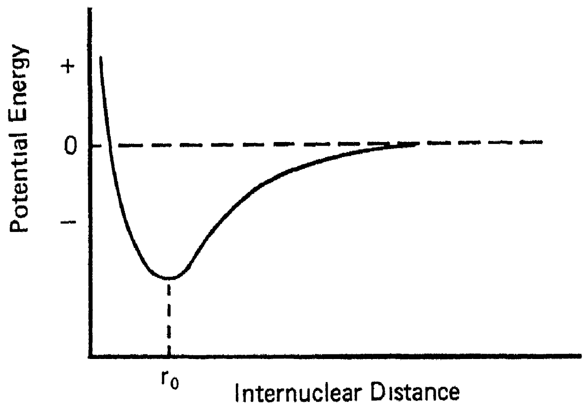
A-5 Increases. (A positive potential energy indicates repulsion.)

Q-6 A plot of potential energy vs. internuclear distance for the attractive and repulsive forces between atoms is given below.



Draw the curve resulting from the interaction of the attractive and repulsive forces. This new potential energy curve represents the bond energy between two nuclei as a function of internuclear distance.

A-6



Q-7 What does the minimum in the curve (r_0) represent?

A-7 The minimum represents the internuclear distance at which the potential energy of the system is the lowest At this distance the attraction between the atoms is the greatest This distance (r_0) is called the equilibrium bond distance.

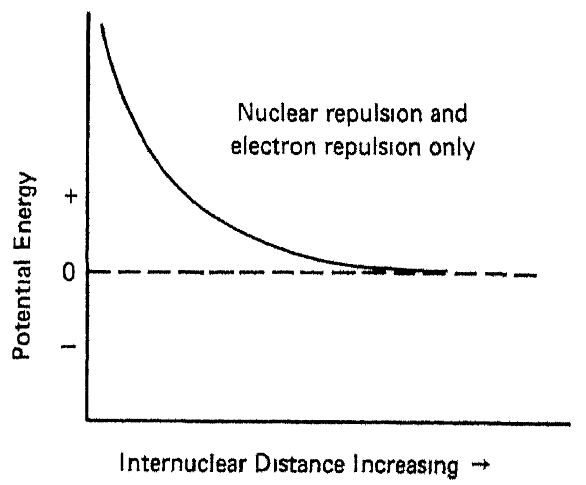
Q-8 How does potential energy relate to the stability of a bond?

A-8 The lower the potential energy the greater the stability of the bond.

Q-9 What would you expect a diagram of potential energy vs internuclear distance to look like for the system where the spins of the electrons are identical?

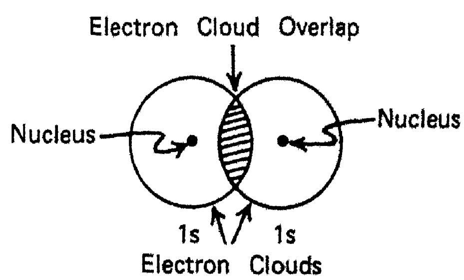
(Hint: Are there any attractive forces?)

A-9 No bonding occurs (no orbital overlap), therefore, no attractive forces



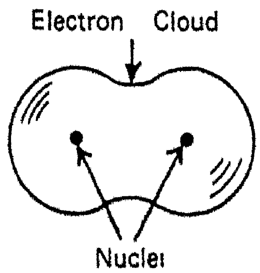
Q-10 A simple example of a covalent bond is the hydrogen molecule. Illustrate the overlap of the 1s orbitals in the diatomic hydrogen molecule.

A-10



Q-11 The electron cloud overlap leads to a greater electron density between the two nuclei, indicating that the electrons are localized there. Draw a boundary diagram (boundary which contains 99% of the electron cloud) for the bonding electrons in the hydrogen molecule.

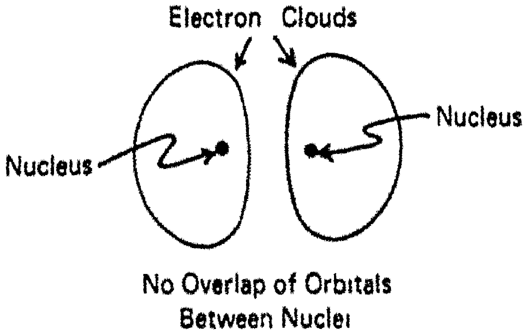
A-11



Q-12 Draw the boundary diagram to illustrate the bonding electrons for the hydrogen molecule when the spins are parallel (the same)

(Hint. Will the 1s orbitals overlap?)

A-12



This is known as an anti-bonding state.

R Bonding occurs between atoms when their electron clouds overlap which permits the exchange of electrons between the atoms.

S-2 The valence of an atom (the number of bonds it forms) is determined by the number of unpaired electrons. Each orbital containing an unpaired electron can overlap an orbital of another atom containing an unpaired electron to form a covalent bond. Consider the molecule PH_3. The electronic configuration of phosphorus is $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p_x^1$ $3p_y^1$ $3p_z^1$. Phosphorus has three 3p orbitals available to form covalent bonds with hydrogen atoms whose electronic configuration is $1s^1$. One representation of the bonding is called the <u>valence bond description</u> and is illustrated for PH_3 in the following manner:

$$P\left\{\underset{3s}{\underline{\uparrow\downarrow}}\quad \boxed{\underset{3p}{\underline{\uparrow}}}\quad \boxed{\underset{3p}{\underline{\uparrow}}}\quad \boxed{\underset{3p}{\underline{\uparrow}}}\right\}$$

$$H\left\{\boxed{\underset{1s}{\underline{\downarrow}}}\right\},\ H\left\{\boxed{\underset{1s}{\underline{\downarrow}}}\right\},\ H\left\{\boxed{\underset{1s}{\underline{\downarrow}}}\right\}$$

Only the valence electrons need to be shown since electrons in inner shells do not take part in bonding.

Q-13 Illustrate the valence bond description for bonding in the molecule Br_2. Which orbitals overlap to form the bond?

A-13

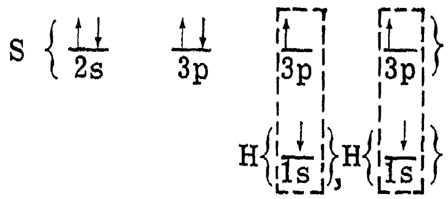
$$Br\left\{\underset{4s}{\underline{\uparrow\downarrow}}\quad \underset{4p}{\underline{\uparrow\downarrow}}\quad \underset{4p}{\underline{\uparrow\downarrow}}\quad \boxed{\underset{4p}{\underline{\uparrow}}}\right\}$$

$$Br\left\{\underset{4s}{\underline{\uparrow\downarrow}}\quad \underset{4p}{\underline{\uparrow\downarrow}}\quad \underset{4p}{\underline{\uparrow\downarrow}}\quad \boxed{\underset{4p}{\underline{\downarrow}}}\right\}$$

The $4p^1$ orbitals overlap.

Q-14 Give the valence bond representation for bonding in the molecule H_2S. Which orbitals overlap to form the bond?

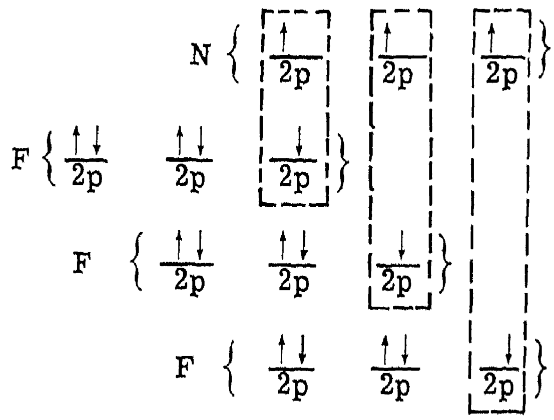
A-14



The $1s^1$ orbital of hydrogen overlaps the $3p^1$ orbitals of sulfur

Q-15 Give the valence bond representation for bonding in the molecule NF_3 Which orbitals overlap to form the bonds?

A-15

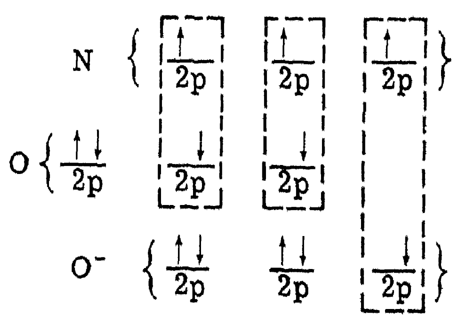


Since the 2s electrons are not involved in bonding, they do not have to be included in the representation

The $2p^1$ orbitals of nitrogen and $2p^1$ orbitals of fluorine overlap

Q-16 Give the valence bond representation for bonding in the ion NO_2^- Which orbitals overlap to form the bonds?

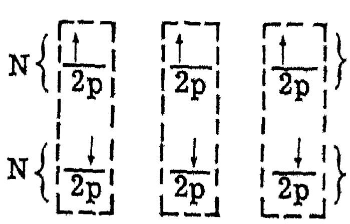
A-16



The $2p^1$ orbitals of oxygen overlap the $2p^1$ orbitals of the nitrogen. There is a double bond between nitrogen and one oxygen

Q-17 Give the valence bond representation for bonding in the molecule N_2.

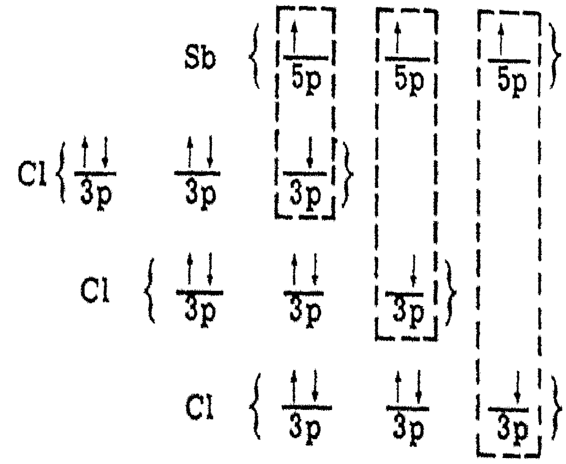
A-17



There is a triple bond between the two nitrogen atoms.

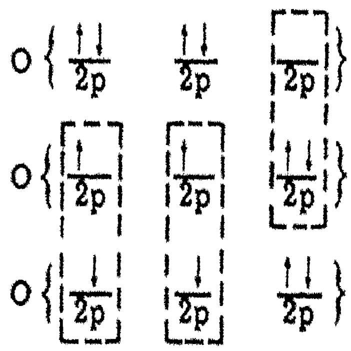
Q-18 Give the valence bond representation for bonding in the molecule $SbCl_3$.

A-18



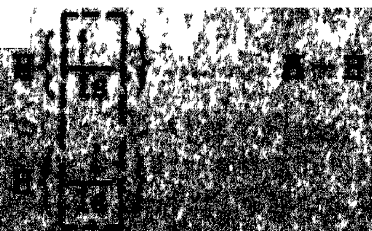
Q-19 Give the valence bond representation for bonding in the molecule O_3

A-19



There is one double bond and one single bond between the three oxygen atoms.

The valence bond representation for bonding illustrates the sharing of electrons in overlapped orbitals.
Example: H_2 molecule



S-3 An important extension of the valence bond theory is given by the following postulates.

a) bond angles can be approximated from directional characteristics of orbitals
b) the strongest bond will be formed between the orbitals of two atoms that overlap to the maximum extent
c) the direction of the bond formed will be in the direction in which the orbitals are concentrated

Q-20 What are the directional properties of s orbitals? Directional properties of atomic orbitals were given in Chapter 3.

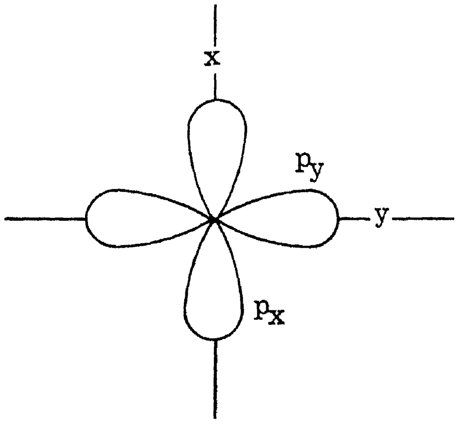
A-20 No directional properties. The charge distribution is spherically symmetrical.

Q-21 What are the directional properties of p orbitals?

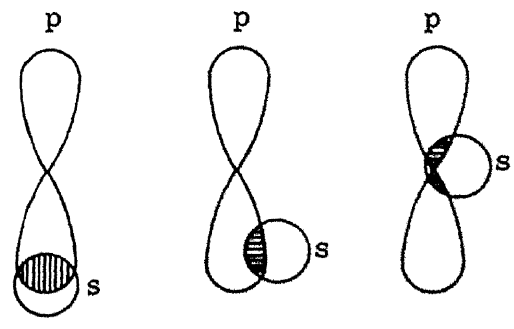
A-21 Their maximum electron density is along the mutually perpendicular coordinate axes.

Q-22 Show the directional properties for the $2p_x$ and $2p_y$ orbitals.

A-22



Q-23 Which orbital overlap would give the strongest bond? Why?

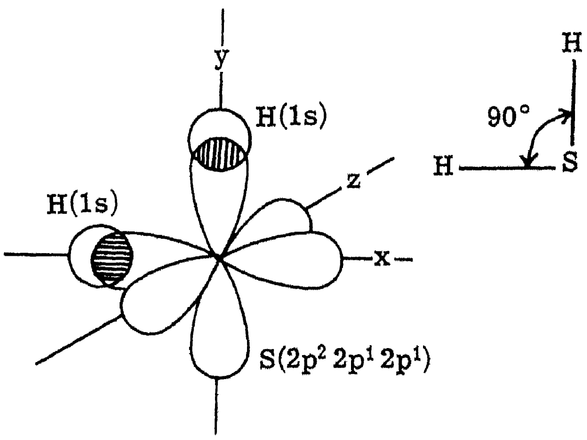


(a) (b) (c)

A-23 (a) The orbitals overlap to the greatest extent

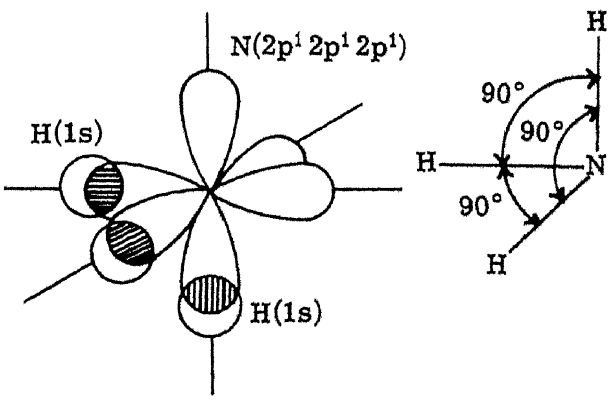
Q-24 Illustrate what would be predicted for the H—S—H bond angles in H_2S. Why?

A-24 Bond angles = 90° The p orbitals in sulfur that are taking part in bonding are at right angles to each other.



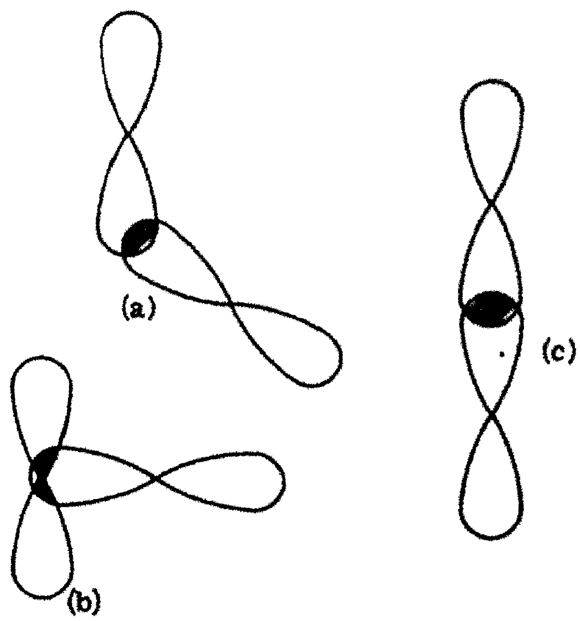
Q-25 Illustrate what would be predicted for the H - N - H bond angle in NH_3. Why?

A-25 90°. p orbitals of nitrogen overlap with the s orbitals of hydrogen.



Actually the bond angle is larger - 107°. This will be discussed later on.

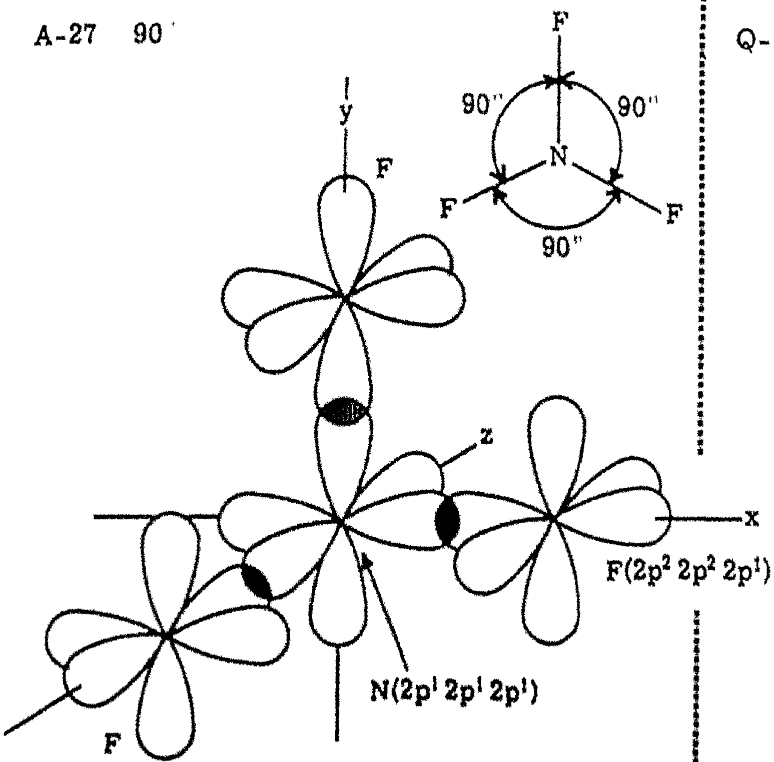
Q-26 Which orbital overlap would give the strongest bond? Why?



A-26 (c). The orbitals overlap to a greater extent and the direction of the overlap is in the direction in which the orbitals are concentrated.

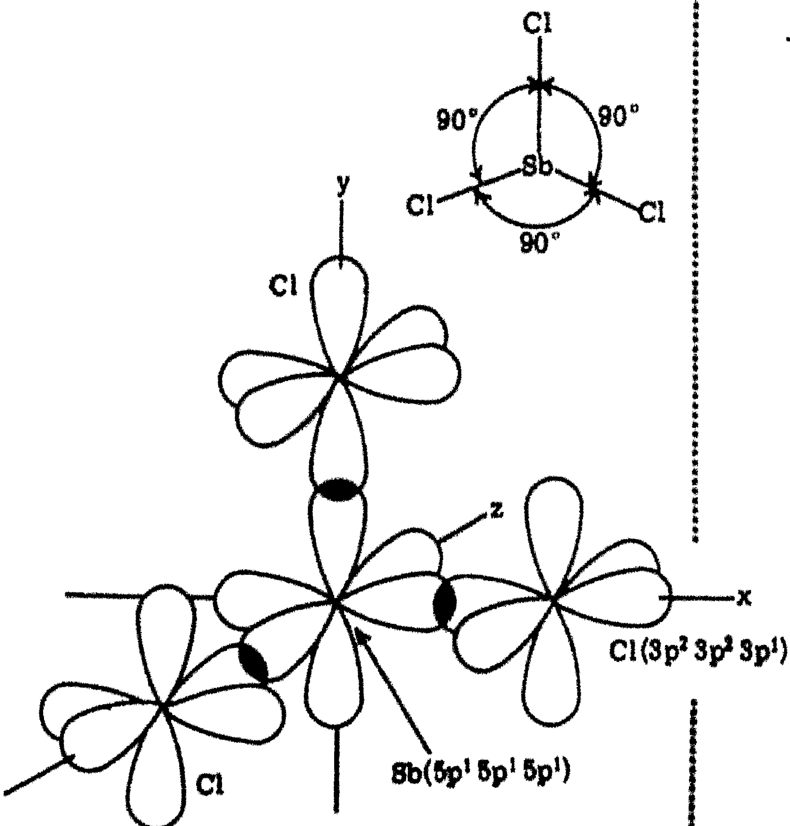
Q-27 Assuming the 3 unpaired electrons of N were in p orbitals, illustrate what would be predicted for the F—N—F bond angle in NF_3. See A-15

A-27 90°



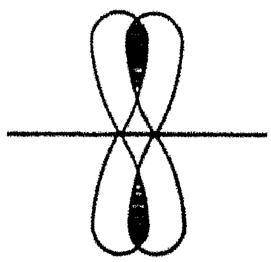
Q-28 Illustrate what would be predicted for the Cl-Sb—Cl bond angle in $SbCl_3$ See A-18

A-28 90°

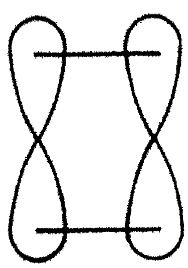


Q-29 Besides overlapping end to end

p orbitals can overlap side to side.

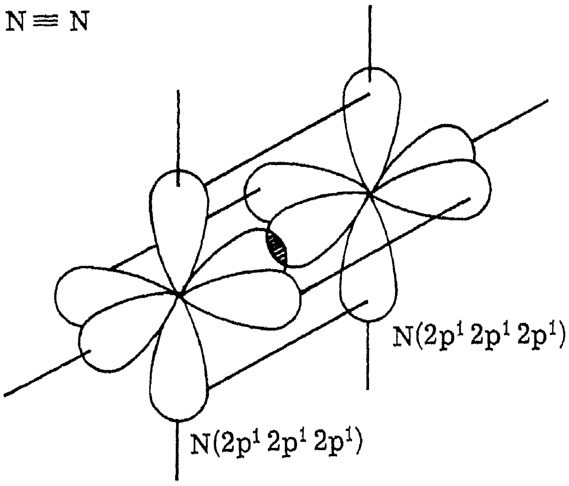


This type of p orbital overlap occurs whenever multi-bonding (double, triple) occurs between two atoms and is called π bonding. Illustrate the bonding in the N_2 molecule. (See A-17.) Use the symbol



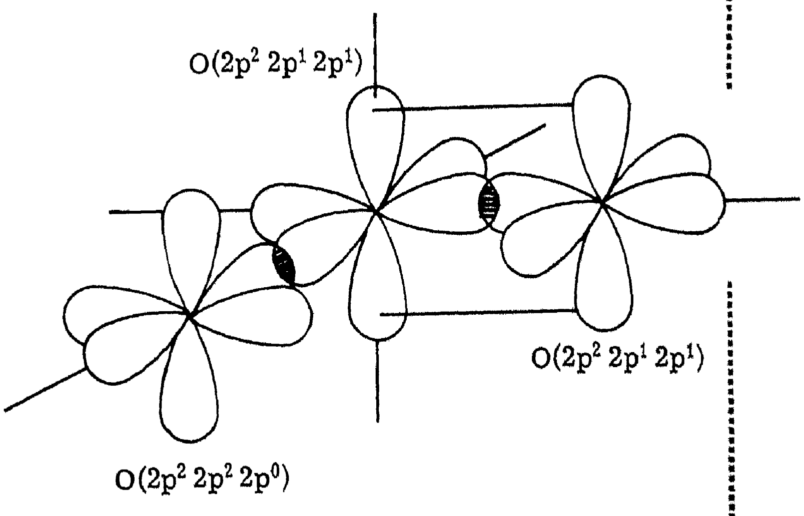
to represent side to side overlap of p orbitals.

A-29 N≡N



Q-30 Illustrate what would be predicted for the O—O—O bond angle in the O_3 molecule See A-19

A-30 90°



No other structure would be valid because it would place more than two electrons in any one orbital

Q-31 How many electrons does Be have available for bonding? Illustrate by giving the electronic configuration for Be.

A-31 Be($1s^2$, $2s^2$). According to the valence bond theory there would be no orbitals with unpaired electrons available for bonding.

Q-32 Experimentally it is known that Be forms two covalent bonds, such as in the molecule BeF_2. Explain how this might be possible.

(Hint: How many half-filled orbitals must Be have?)

A-32 One of the 2s electrons can be excited into a higher energy orbital (2p) This would give Be the electronic configuration of $1s^2$, $2s^1$ $2p^1$. It would have two half-filled orbitals available for bonding

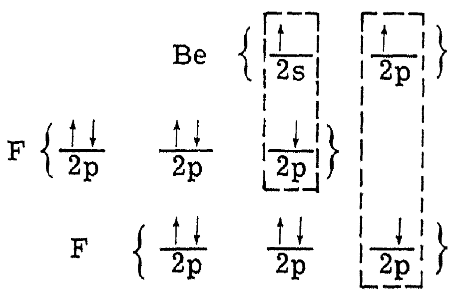
Q-33 What are the energy requirements for Be forming the electron configuration of $1s^2$, $2s^1$ $2p^1$? Why might this be possible when forming bonds?

(Hint: Energy is released in bond formation.)

A-33 Energy is necessary to excite the electron into a higher energy orbital The energy released in forming two chemical bonds more than compensates for the energy needed for electron promotion

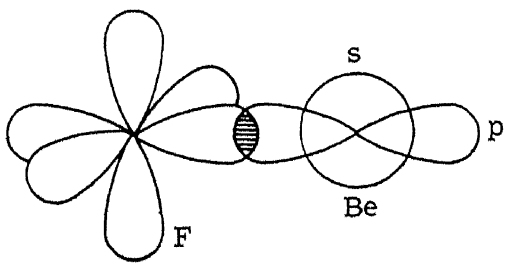
Q-34 Give the valence bond representation for bonding in the BeF_2 molecule

A-34



Q-35 Illustrate orbital overlap for bonding in BeF_2 What would be predicted for the F—Be—F bond angle?

A-35

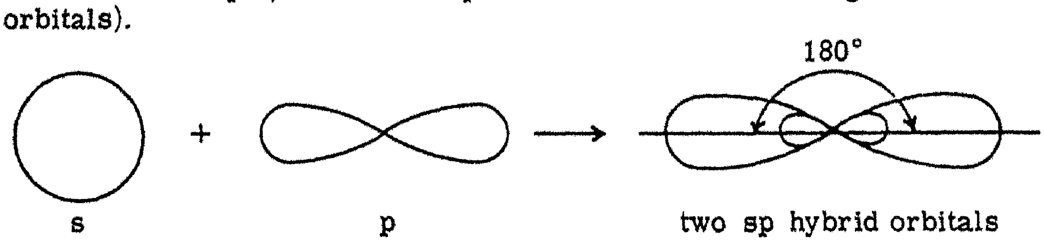


The other F atom would overlap the 2s orbital of Be. Most likely the second F atom would bond at 90° to the first F atom. This is <u>not</u> the observed bond angle, however

R **The geometry of a molecule can be approximated from the directional properties of atomic orbitals and their maximum overlap in bond formation.**

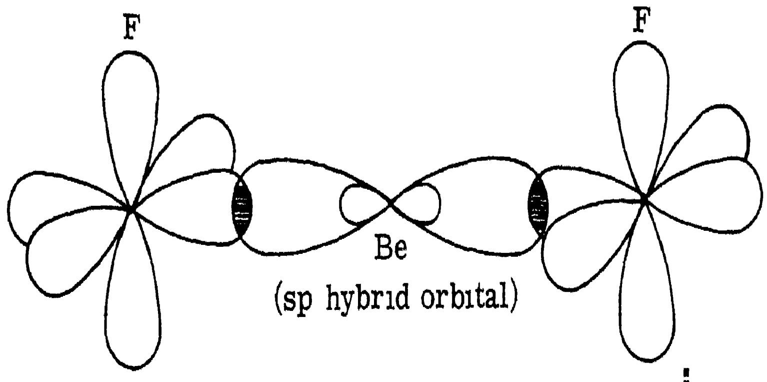
PART III: Hybridization

S-1 To account for the discrepancy between the predicted and observed bond angles in molecules like NH_3 and BeF_2, a process called <u>hybridization</u> has been suggested. Hybridization is the mixing of pure orbitals to form new orbitals which are <u>equivalent</u> and have definite orientations in space For example, an s and a p orbital could combine to give two new orbitals (called sp orbitals).



Q-1 If Be hybridized an s and a p orbital in the formation of BeF_2, draw a picture illustrating the bonding.

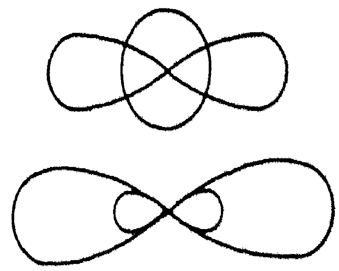
A-1 F—Be—F



Q-2 What is the F—Be—F bond angle for the molecule represented in A-1?

A-2 180° (This would be true for bonds formed with any sp hybridized atom.)

Q-3 It is important to note that a hybridized orbital, because of its directional qualities, extends out farther in space than the pure orbitals.



Can you give a reason for hybridization occurring even thought it takes energy for electrons to be promoted into hybridized orbitals?

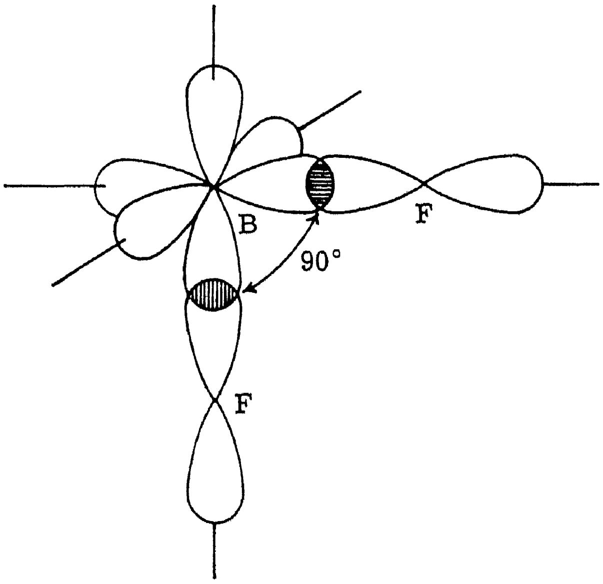
A-3 Hybrid orbitals can overlap more effectively than pure orbitals because of their greater extension in space. This increased overlap results in a more stable bond which compensates for the energy needed to promote electrons into hybridized orbitals.

Q-4 In order for B to form three covalent bonds in the BF_3 molecule, how must the electronic structure of boron in the ground state be changed?

A-4 B ($1s^2$, $2s^1$ $2p^1$ $2p^1$). An s electron is promoted to a p orbital, giving three valence electrons suitable for bond formation.

Q-5 The F—B—F bond angle in BF_3 is 120° for each bond. Is there any way you can account for this by using pure s and p orbitals?

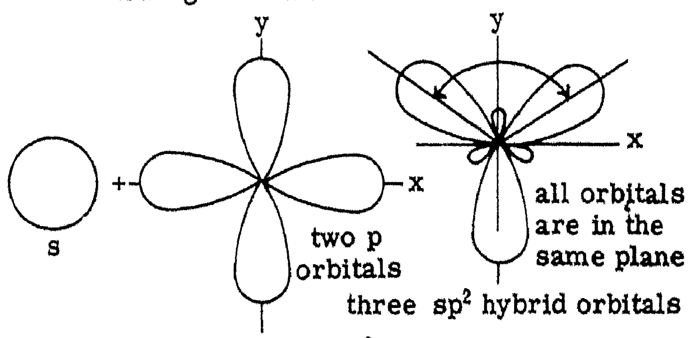
A-5 No The use of two pure p orbitals would mean that at least one bond angle would be 90°



Q-6 If pure p orbitals were used in forming the B-F bonds in BF_3, angles of 90° would be expected The actual observed bond angles are 120° What concept might be useful in explaining the observed angles?

A-6 Hybridization

Q-7 The combination of an s and two p orbitals to form three hybridized sp^2 orbitals can be illustrated in the following manner.

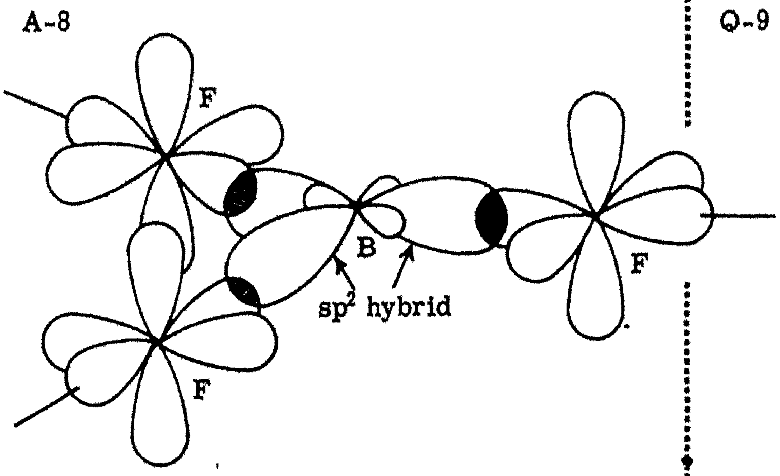


In order for the sp^2 hybridized orbitals to be as far removed from each other as possible, what would be the angle between the orbitals?

A-7 $\frac{360°}{3}$ (for a circle) = 120°

Q-8 If B is hybridized in BF_3, illustrate the bonding in the molecule.

A-8



Q-9 What would be the bond angle for atoms where the central atom is sp^2 hybridized?

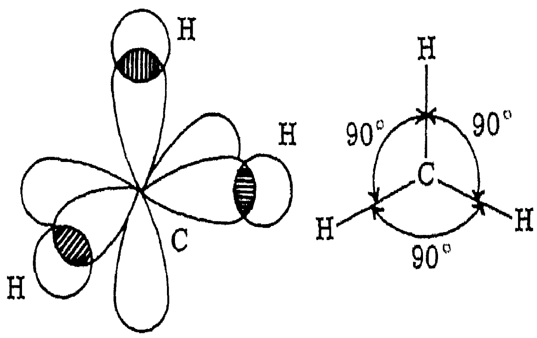
A-9 120°

Q-10 In order for carbon to form four covalent bonds in the CH_4 molecule, how must the ground state electronic configuration for C be changed?

A-10 C ($1s^2$, $2s^1$ $2p^1$ $2p^1$ $2p^1$) An s electron is promoted to a p orbital giving four valence electrons suitable for bond formation

Q-11 The H C H bond angles in the CH_4 molecule are 109° each. Is there any way you can account for this by using pure s and p orbitals?

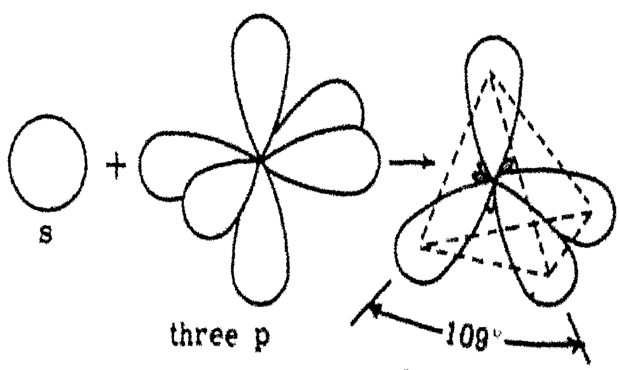
A-11 No The use of the pure p orbitals would give at least two 90° bond angles



Q-12 If pure p orbitals were used in forming the C H bonds in CH_4, angles of 90 would be expected The observed bond angles are 109° each. What concept might be useful in explaining the observed angles?

A-12 Hybridization

Q-13 The combination of an s and three p orbitals to form four hybridized sp^3 orbitals can be illustrated in the following manner.



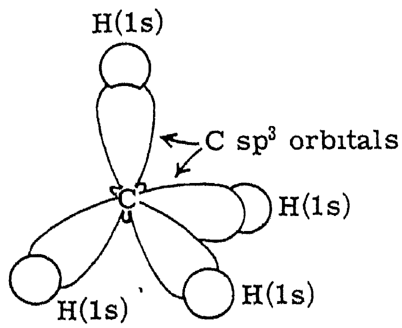
four sp^3 hybrid orbitals

Why is the angle between the hybridized orbitals 109° ?

A-13 It is this geometry in space which keeps the orbitals as far removed from one another as possible.

Q-14 The sp^3 orbitals are directed to the corners of a regular tetrahedron. If the carbon atom in CH_4 is hybridized, illustrate the bonding in the molecule.

A-14



Q-15 What would be the bond angle for atoms where the central atom is sp^3 hybridized?

A-15 109°

Q-16 Of the three types of hybrid orbitals, sp, sp^2, and sp^3, which has the most s character? In other words, which hybridized orbital has the greatest percentage of s orbital?

A-16 sp contains 50% s character

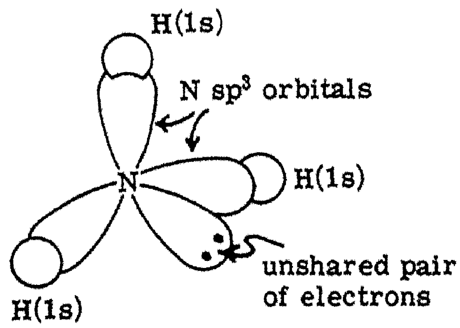
Q-17 As the s character of a hybridized orbital decreases, what happens to the bond angle?

A-17 It decreases.

sp	180°
sp^2	120°
sp^3	109°
p	90°

Q-18 If the nitrogen atom in the NH_3 molecule is sp^3 hybridized, illustrate the bonding in this compound (Include unshared pairs of electrons in the valence shell.) What would be the H—N—H bond angle?

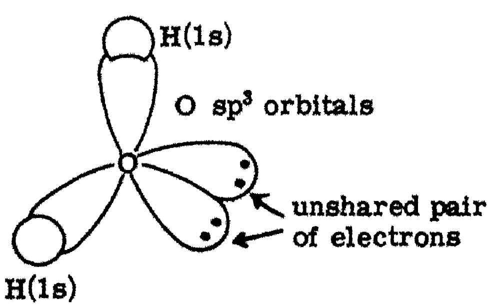
A-18



Predicted Bond Angle - 109°
(Experimental 108°)

Q-19 If the oxygen atom in the H_2O molecule is sp^3 hybridized, illustrate the bonding in the compound. (Include unshared pairs of electrons in the valence shell.) What is the predicted H—O—H bond angle?

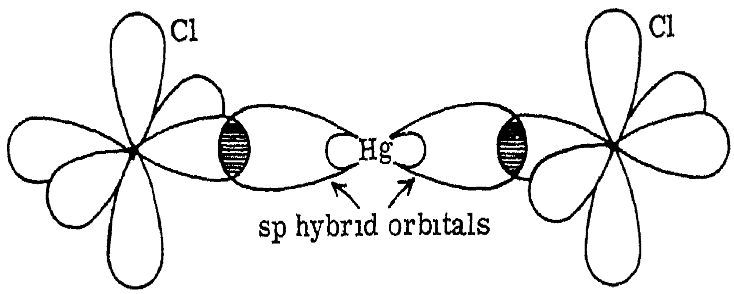
A-19



Predicted Bond Angle - 109°
(Experimental 105°)

Q-20 If the Hg atom in the $HgCl_2$ molecule is sp hybridized, illustrate the bonding in this compound. What is the predicted Cl—Hg—Cl bond angle?

A-20 Bond angle 180°



Q-21 In the BH_3 molecule the H—B—H bond angle is 120°. What kind of hybridization is likely?

A-21 sp^2

Q-22 The Cl—Sb—Cl bond angle in $SbCl_3$ is 109°. What type of hybridization would account for this angle?

A-22 sp^3

Q-23 The $CdBr_2$ molecule has a Br—Cd—Br bond angle of 180°. What type of hybridization would account for this angle?

A-23 sp

Q-24 The SO_3 molecule is planar with O—S—O bond angles of 120°. What type of hybridization would account for this angle?

A-24 sp^2

Q-25 If the As atom in the AsH_3 molecule is sp^3 hybridized, what would be the H—As—H bond angle?

A-25 109°

Q-26 If the Zn atom in the ZnI_2 molecule is sp hybridized, what would be the I—Zn—I bond angle?

A-26 180°

Q-27 If the N atom in the NO_3^- ion is sp^2 hybridized, what would the O—N—O bond angle be?

A-27 120°

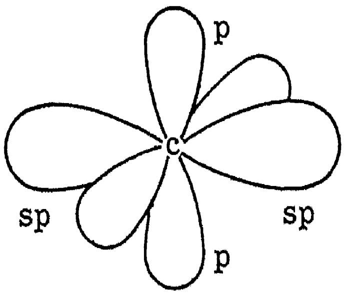
S-2 Some atoms may be hybridized in more than one way. Carbon hybridizes to form the following orbitals

sp^3

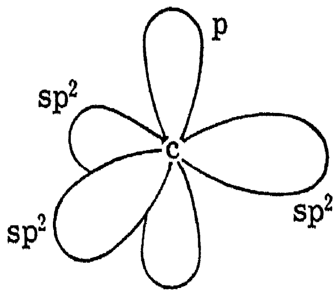
sp^2 (plus one p orbital)

sp (plus two p orbitals)

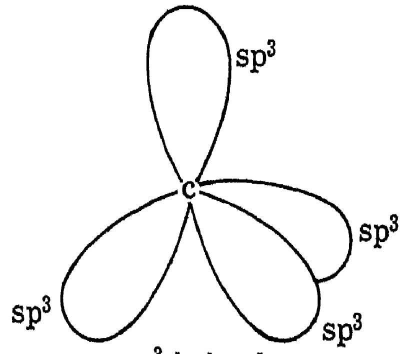
These orbitals are illustrated on the following page.



sp hybrid



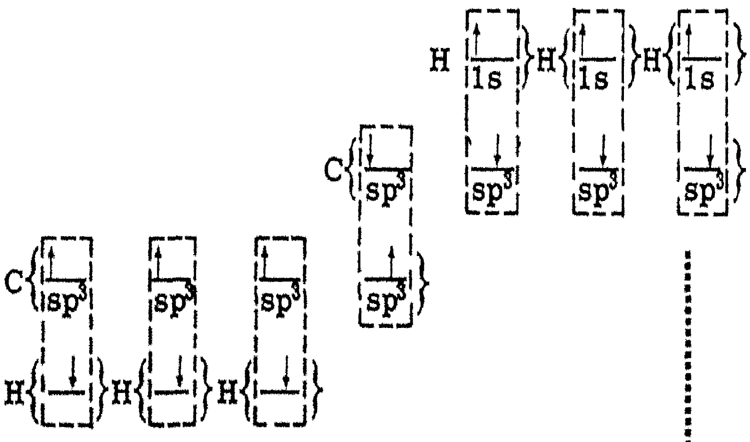
sp^2 hybrid



sp^3 hybrid

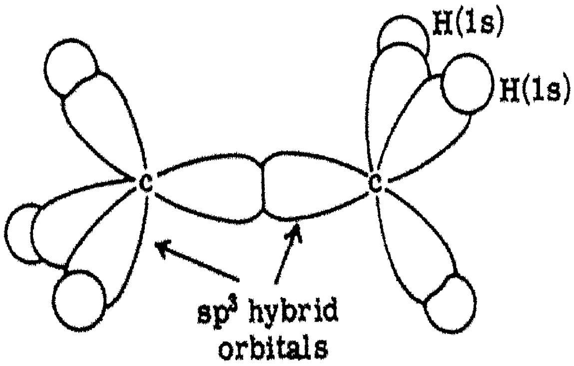
Q-28 In C_2H_6, the C atoms are sp^3 hybridized Give the valence bond representation for bonding in C_2H_6.

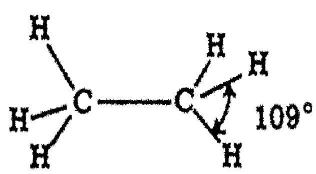
A-28



Q-29 Illustrate the bonding in the C_2H_6 molecule

A-29



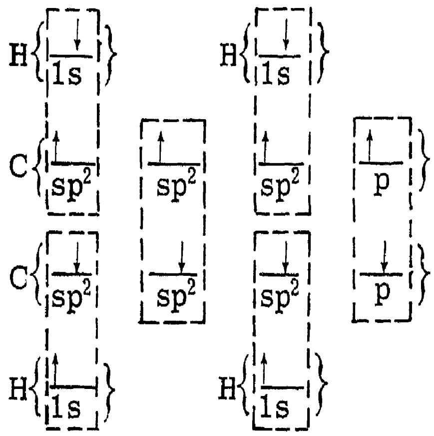


Q-30 What type of hybridization would account for the fact that all bond angles in C_2H_4 are 120° ?

A-30 sp^2

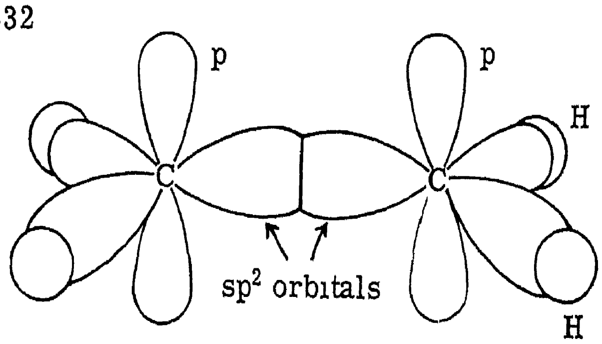
Q-31 Indicate a valence bond representation for the bonding in C_2H_4.

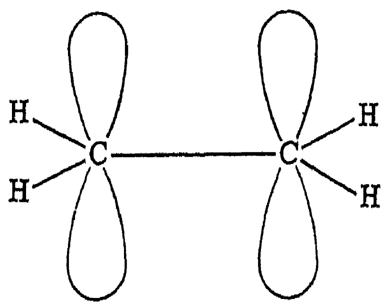
A-31



Q-32 Draw an orbital picture of the C_2H_4 molecule showing how sp^2 orbitals might bond

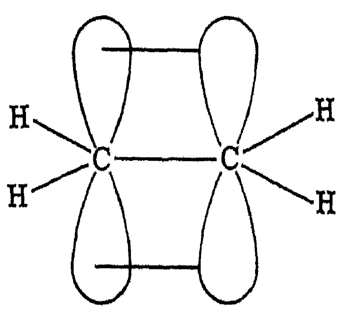
A-32

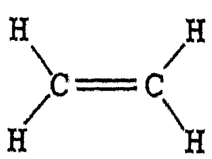




Q-33 If the C—C bond distance were shorter in the picture given for the C_2H_4 molecule, what other orbitals might overlap? Illustrate.

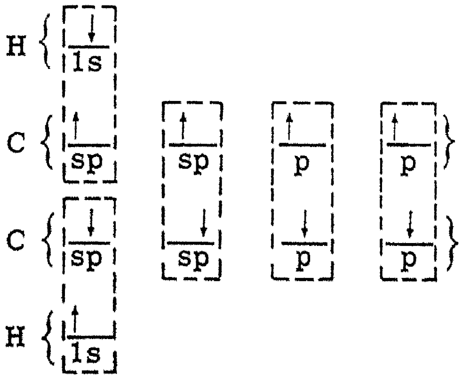
A-33 The pure p orbitals may overlap sideways forming a π bond





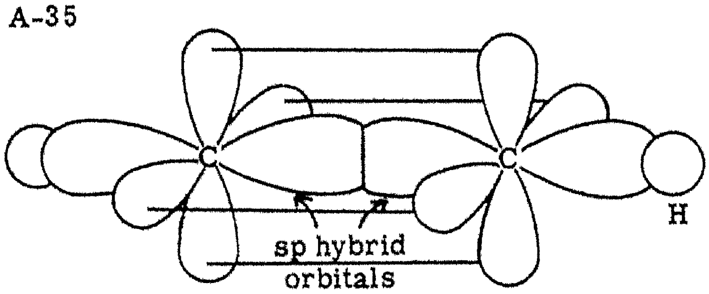
Q-34 Give the valence bond representation for the bonding in the C_2H_2 molecule where all the bond angles are 180°.

A-34 Carbon is sp hybridized



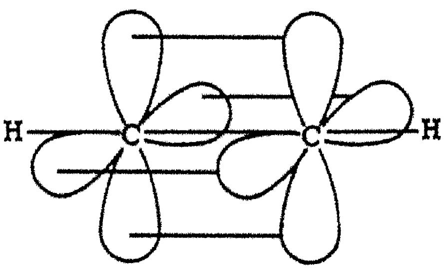
Q-35 Draw an orbital picture of the bonding in the C_2H_2 molecule

A-35



Two pairs of p orbitals overlap sideways to form two π bonds.

Two alternative ways to represent C_2H_2 are



$H-C\equiv C-H$

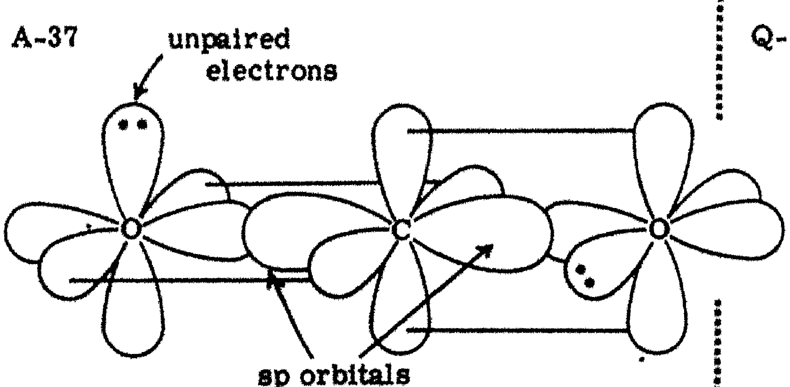
Q-36 The bond angle in the CO_2 molecule is 180° What type of hybridization would account for this bond angle?

A-36 sp

Q-37 Draw an orbital picture of the bonding in the CO_2 molecule.

(Hint. Consider C as being sp hybridized.)

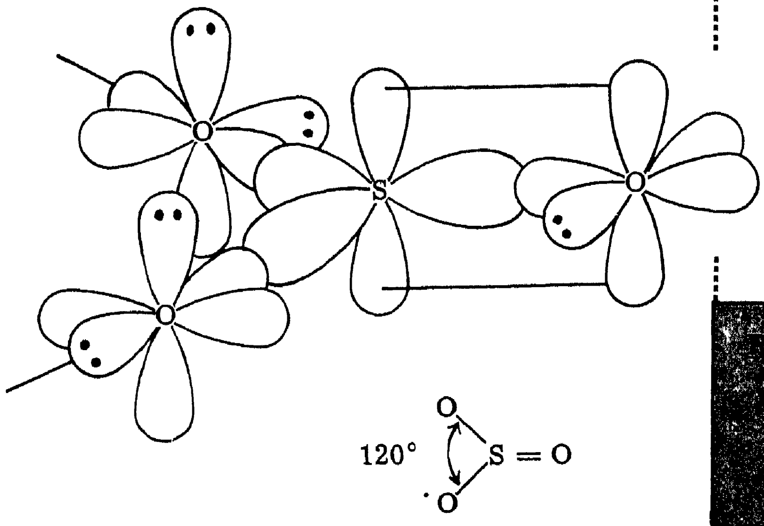
A-37



$\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$

Q-38 The bond angles in the SO_3 molecule are 120°. Illustrate the bonding in this compound.

A-38



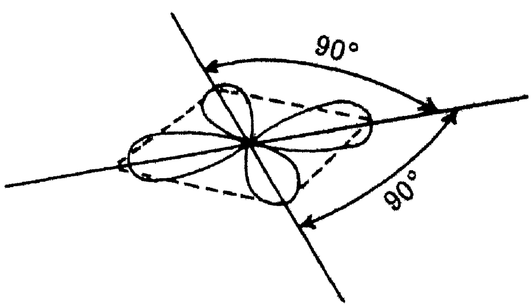
S-3 Elements in the third period and beyond, where d orbitals begin to become involved in bonding, may form two new types of hybrid orbitals. Pure d, p and s orbitals mix together to form dsp^2 and d^2sp^3 hybridized orbitals.

Q-39 In the dsp^2 hybridized orbitals, what pure orbitals are combined to form hybrid orbitals and how many hybrid orbitals are formed?

A-39 One s, one d, two p orbitals are combined They form four equivalent orbitals that are coplanar and at right angles to one another. Each orbital has the shape illustrated below.

Q-40 The dsp^2 hybrid orbitals are coplaner and at right angles to one another. Draw a diagram to illustrate the geometry of the dsp^2 hybridized orbitals.

A-40

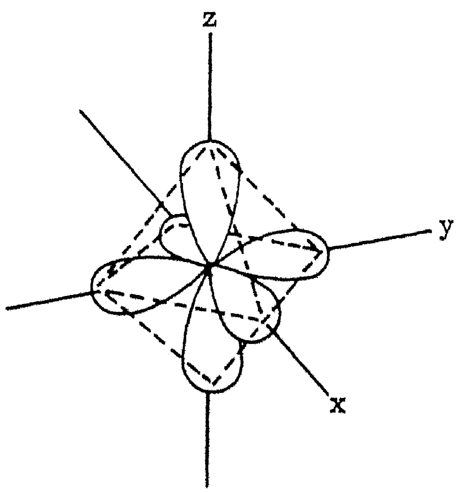


Q-41 In the d^2sp^3 hybridized orbitals, what pure orbitals are combined, and how many hybridized orbitals are formed?

A-41 One s, two d, three p orbitals are combined They form six equivalent orbitals which are directed toward the apices of a regular octahedron. Each orbital has the shape illustrated below.

Q-42 The d^2sp^3 hybrid orbitals are directed toward the apices of a regular octahedron. Illustrate the geometry of the d^2sp^3 hybridized orbitals.

A-42



Q-43 Give the electronic configuration for Ni^{+2} (Remember when electrons are lost to form ions, they are lost from the outermost energy level)

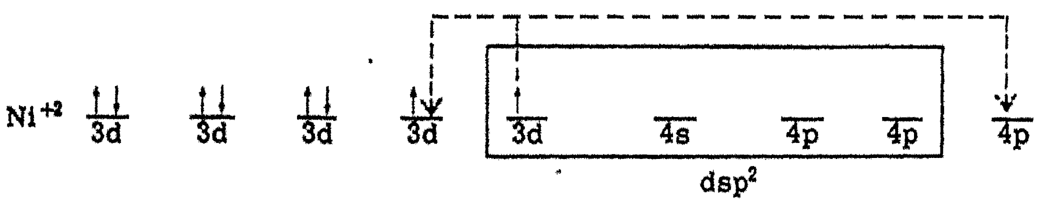
A-43 Ni^{+2} ($1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^2$ $3d^2$ $3d^2$ $3d^1$ $3d^1$)

The two 4s electrons are lost on ionization.

Q-44 In the complex ion $[Ni(CN)_4]^{-2}$, each CN^- ion donates a pair of electrons to an empty orbital of the Ni^{++} ion. If the four empty orbitals in the Ni^{++} ion are a 3d, a 4s and two 4p orbitals, how must the electronic structure of Ni^{++} ion given in A-43 be modified?

A-44 Since each CN^- donates two electrons for bond formation, Ni^{+2} must have one d, one s and two p orbitals empty for dsp^2 hybridization. This can be done by pairing up all the 3d electrons or by exciting a 3d electron into a 4p orbital.

Q-45 If the complex ion $[Ni(CN)_4]^{-2}$ is dsp^2 hybridized, how can it be determined if the ion has a $4p^1$ structure

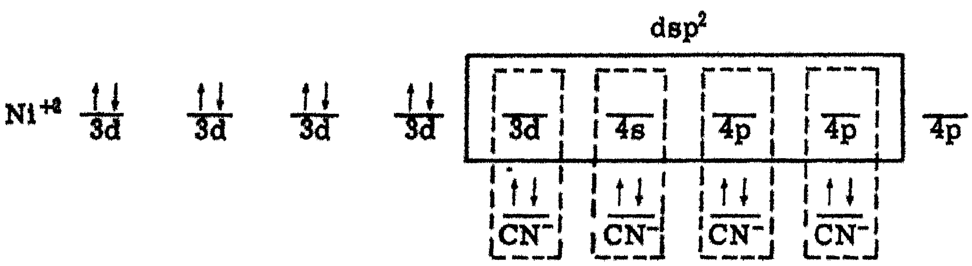


A-45 Determine if the ion is paramagnetic or diamagnetic. If it is diamagnetic, all the electrons in the ion are paired.

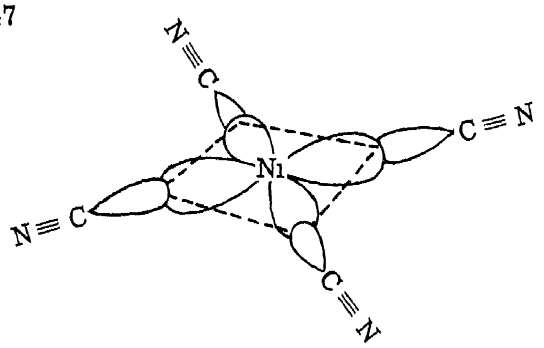
Q-46 Given that the $[Ni(CN)_4]^{-2}$ ion is <u>diamagnetic</u>, illustrate the valence bond representation for the bonding in the ion. (Consider $(CN)^-$ as a unit with an unshared pair of electrons.)

A-46

Q-47 If the carbon atom in the CN^- radical is sp hybridized, illustrate the bonding in the $[Ni(CN)_4]^{-2}$ ion.



A-47



Q-48 What is the C—Ni—C bond angle? What is the Ni—C—N bond angle?

A-48 C—Ni—C = 90°
Ni—C—N = 180°

Q-49 Give the electronic configuration for Cu^{+2}

A-49 Cu^{+2} ($1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^2$ $3d^2$ $3d^2$ $3d^2$ $3d^1$)

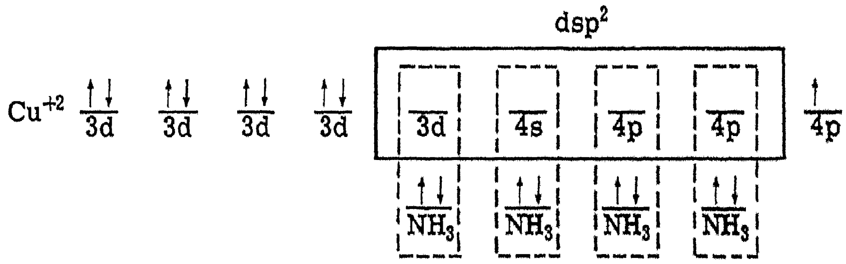
Q-50 In the complex ion $[Cu(NH_3)_4]^{+2}$ the Cu atom is dsp^2 hybridized Explain, in terms of the electronic structure of Cu^{+2}, how this type of bonding can occur. (Each NH_3 molecule donates two electrons to form a coordinate covalent bond.)

A-50 Cu^{+2} must have one d, one s and two p orbitals empty for dsp^2 hybridization This can be arranged by promoting a 3d electron into a 4p orbital

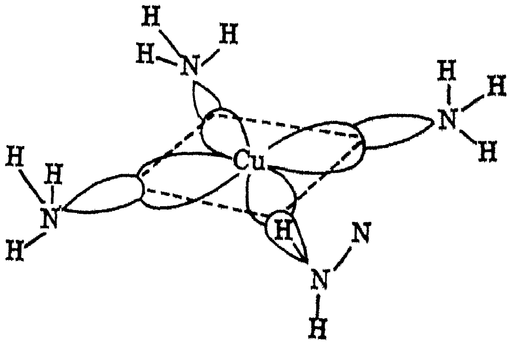
Q-51 Give the valence bond representation for the bonding in the $[Cu(NH_3)_4]^{+2}$ ion. (Consider NH_3 as a unit with an unshared pair of electrons.)

A-51

Q-52 If the N atom in NH_3 is tetrahedrally hybridized, illustrate the bonding in the $[Cu(NH_3)_4]^{+2}$ ion.



A-52



Q-53 What is the N—Cu—N bond angle? What is the Cu—N—H bond angle?

A-53 N—Cu—N = 90°
Cu—N—H = 109°

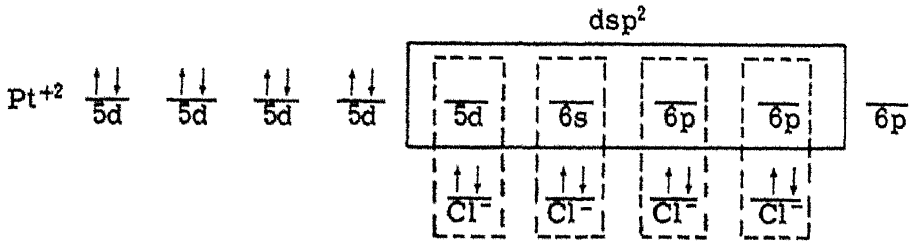
Q-54 Is the $[Cu(NH_3)_4]^{+2}$ ion paramagnetic or diamagnetic? Why?

A-54 Paramagnetic, because it has one unpaired electron.

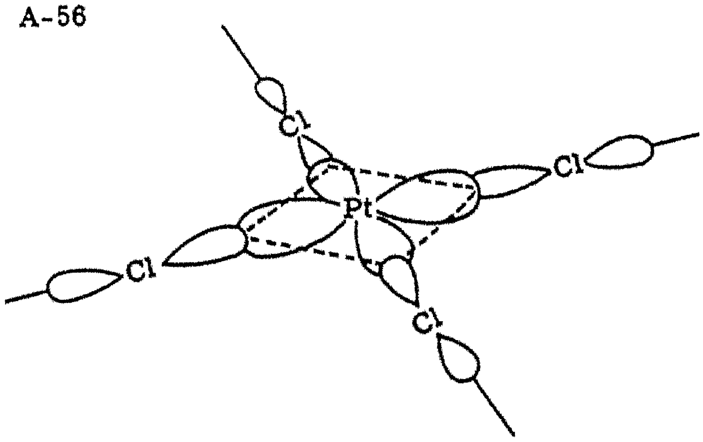
Q-55 Give the valence bond representation for the bonding in the diamagnetic $[PtCl_4]^{-2}$ ion (Pt is dsp^2 hybridized Each Cl^- donates a pair of electrons)

A-55

Q-56 Illustrate the bonding in the $[PtCl_4]^{-2}$ ion



A-56



Q-57 Give the electronic configuration for Co^{+3}.

A-57 Co^{+3} ($1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^2$ $3d^1$ $3d^1$ $3d^1$ $3d^1$)

The two 4s electrons and one 3d electron are lost.

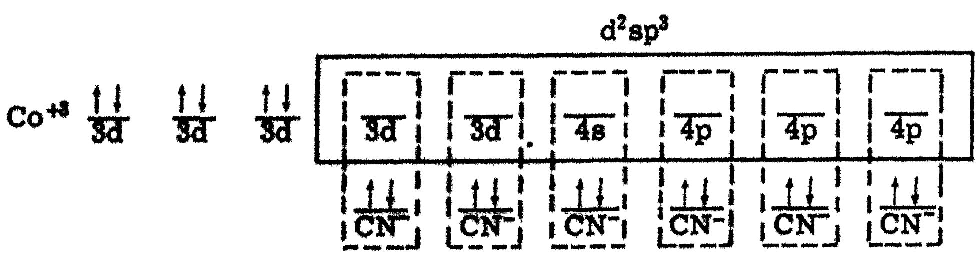
Q-58 In the complex ion, $[Co(CN)_6]^{-3}$, the Co atom is d^2sp^3 hybridized. Explain, in terms of the electronic structure of Co^{+3}, how this type of bonding can occur. (Each CN^- radical donates two electrons to form a coordinate-covalent bond.)

A-58 Co^{+3} must have two d, one s and three p orbitals empty for d^2sp^3 hybridization. This can be arranged by pairing up the 3d electrons.

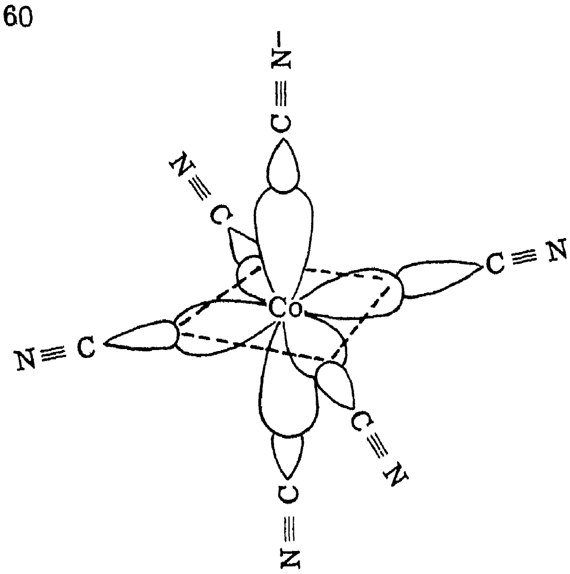
Q-59 Give the valence bond representation for the bonding in the ion $[Co(CN)_6]^{-3}$ assuming that the 3d electrons are paired.

A-59

Q-60 Illustrate the bonding in the ion $[Co(CN)_6]^{-3}$.



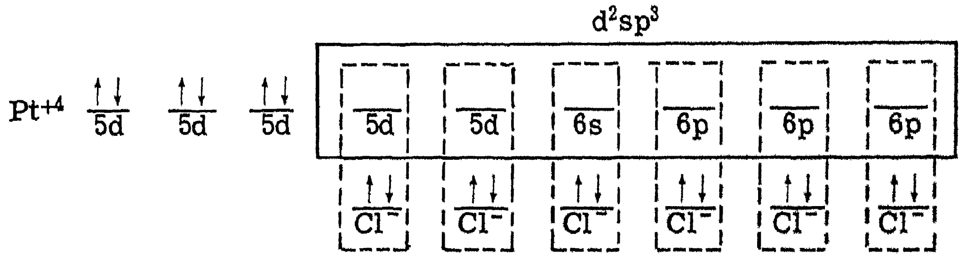
A-60



Q-61 Give the valence bond representation for the bonding in the ion $[PtCl_6]^{-2}$ (Pt is d^2sp^3 hybridized and each Cl^- donates a pair of electrons)

A-61

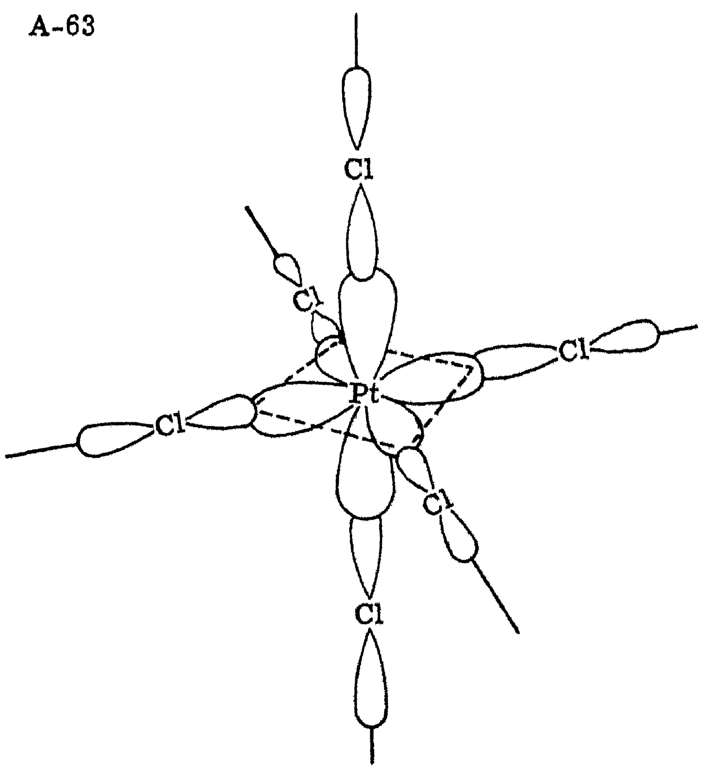
Q-62 What are the magnetic properties of $[PtCl_6]^{-2}$?



A-62 diamagnetic

Q-63 Illustrate the bonding in the ion $[PtCl_6]^{-2}$.

A-63



[redacted]

PART IV: Repulsion Theory

S-1 A simplified concept for determining the geometry of covalent molecules is the Valence-Shell Electron-Pair Repulsion Theory (VSEPRT). This theory is based on the repulsive interactions of pairs of valence electrons. The electron pairs are regarded as occupying localized orbitals which are oriented in space about the completed inner electron energy levels so that the distance between the orbitals is a maximum. In the following questions, K will represent the central atom, X will represent an atom or atoms covalently bonded to the central atom, and P will represent a non-bonding pair of electrons.

Q-1 If an atom has two electrons in its valence shell and is bonded to two other atoms, what will be the value for X and P for the central atom?

A-1 In forming a covalent bond, one electron is used from the central atom and one from the other atom being bonded.

X 2 (Central atom is bonded to two other atoms.)

P 0 (One electron is used from the valence shell in forming each bond. A total of two electrons are used in bonding, leaving no electrons remaining in the valence shell to form non-bonding pairs.)

Q-2 If an atom has 6 electrons in its valence shell and is bonded to two other atoms, what will be the value for X and P for the central atom?

A-2 X = 2

$P = \frac{6-2}{2} = 2$ (Divide by 2 since P represents pairs of electrons.)

Q-3 If an atom has 5 electrons in its valence shell and is bonded to three other atoms, what will be the value of X and P for the central atom?

A-3 X = 3

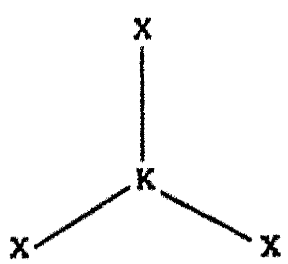
$P = \frac{5-3}{2} = 1$

Q-4 According to the VSEPRT, what geometry should a KX_2 molecule have? (KX_2 does not have any non-bonding electrons.)

A-4 In order for the coulombic repulsion to be minimized, the orbitals containing the valence electrons should be as far away from each other as possible.

X K-X (linear) 180°

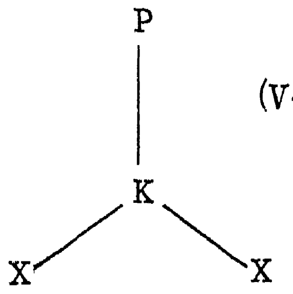
Q-5 What geometry should a KX_3 molecule have?

A-5 

(triangular) 120°

Q-6 What geometry should a KX_2P molecule have?

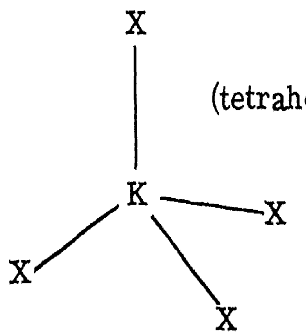
A-6



(V-shaped) 120°

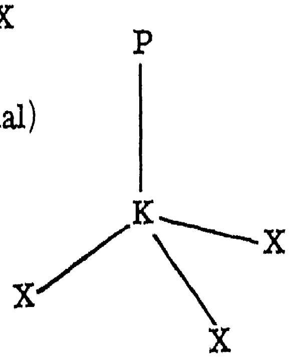
Q-7 What geometry should KX_4, KX_3P, and KX_2P_2 molecules have?

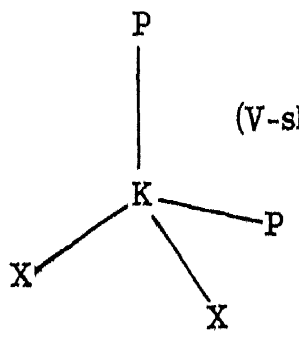
A-7 Minimum repulsion is achieved if orbitals are arranged in a tetrahedral structure



(tetrahedral) 109° 28'

(trigonal pyramidal) 109° 28'





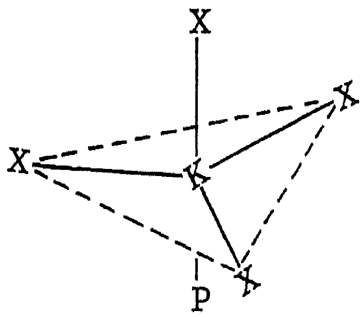
(V-shaped) 109° 28'

R In the Valence-Shell Electron-Pair Repulsion Theory (VSEPRT) electron pairs are regarded as occupying localized orbitals. The orbitals are oriented in space so that the distance between them is at a maximum. (Repulsion is at a minimum.)

S-2 In a valence orbital, the repulsive forces between electrons are greater between two non-bonding pairs of electrons than between a non-bonding pair and a bonding pair. Also, the repulsive forces are greater between a non-bonding pair and a bonding pair than between two bonding pairs of electrons.

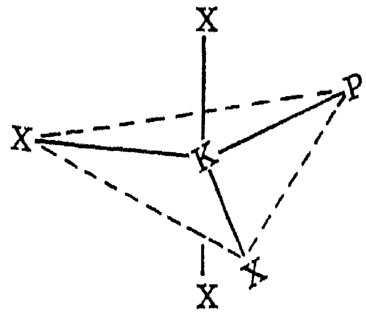
$$P-P > P-X > X-X$$

The most stable structure is the one with minimum repulsion. To decide which arrangement gives the least repulsion, the electron pairs are arranged so that the 90° interactions are at a minimum. The repulsion between electron pairs at angles greater than 90° to each other are ignored. For example, the following structures are possible for KX_4P:



Structure I
90° interactions

P—P 0
P—X 3
X—X 3



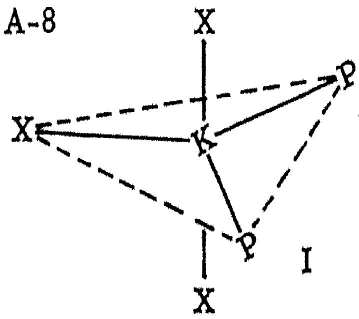
Structure II
90° interactions

P—P 0
P—X 2
X—X 4

In both structures there are six 90° interactions. Since an X—X interaction is weaker than a P—X interaction, structure II has less repulsion and is the more stable structure.

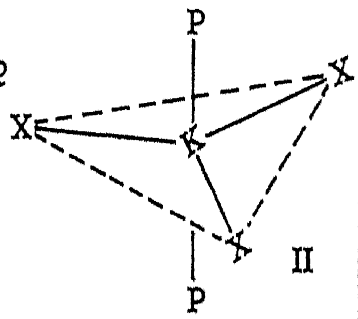
Q-8 Draw the possible structures for KX_3P_2. Indicate the number and kind of 90° interactions.

A-8



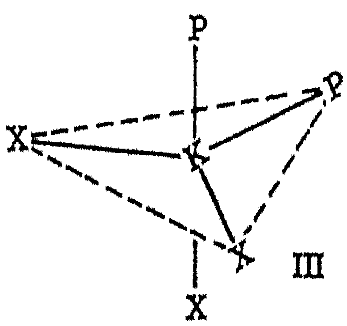
I

P—P 0
P—X 4
X—X 2



II

P—P 0
P—X 6
X—X 0

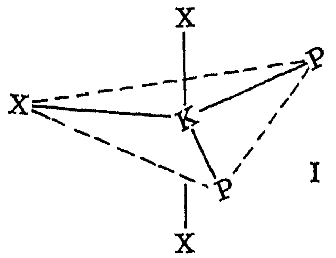


III

P—P 1
P—X 3
X—X 2

Q-9 Which structure in the KX_3P_2 case would be expected to have the minimum repulsion? Why?

A-9

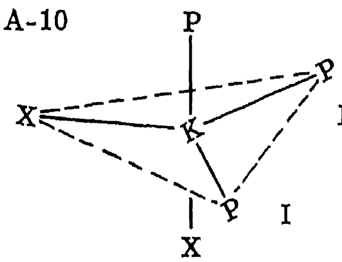


I

In all three structures there are six 90° interactions Since two X—X interactions are weaker than two P—X interactions, structure I is more stable than structure II Because one P—X interaction is weaker than one P—P interaction, structure I is more stable than structure III

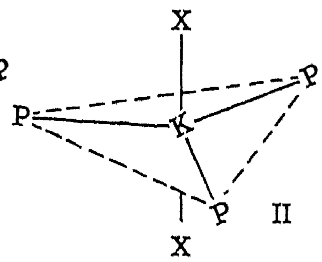
Q-10 Draw the possible structures for KX_2P_3. Indicate the number and kind of 90° interactions

A-10



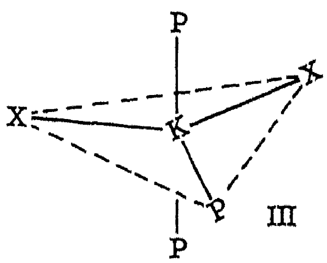
I

P—P	2
P—X	3
X—X	1



II

P—P	0
P—X	6
X—X	0

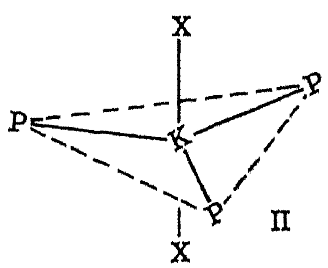


III

P—P	2
P—X	4
X—X	0

Q-11 Which structure in the KX_2P_3 case would be expected to have the minimum repulsion? Why?

A-11

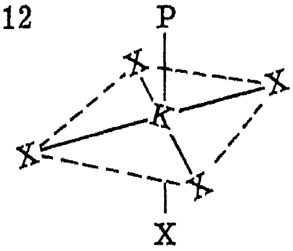


II

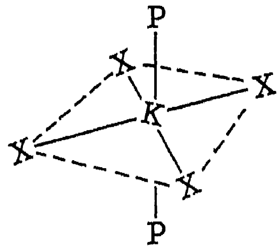
In all three structures there are six 90° interactions Since two P—X interactions are weaker than two P—P interactions, structure II is more stable than structure III. Because three P—X interactions are weaker than two P—P and one X—X interaction, structure II is more stable than structure I.

Q-12 What geometry should KX_5P and KX_4P_2 molecules have?

A-12



square pyramid



square planar

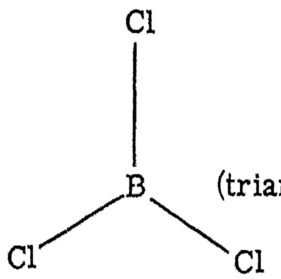
Q-13 Illustrate the molecular shape for the molecule $BeCl_2$

A-13 This would be an example of KX_2

Cl—Be—Cl (linear)

Q-14 Illustrate the molecular shape for the molecule BCl_3

A-14 Example of KX_3



(triangular)

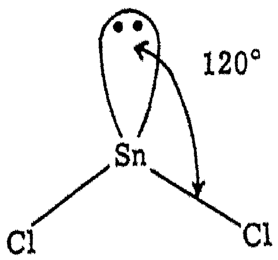
Q-15 Illustrate the molecular shape for the following compounds

a) $SnCl_2$ b) $SnCl_4$ c) NH_3

(Do not count d electrons in determining the number of lone pairs.)

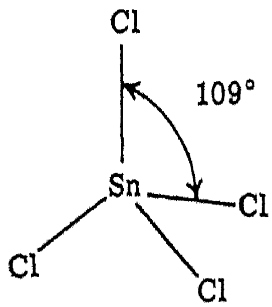
A-15

KX_2P



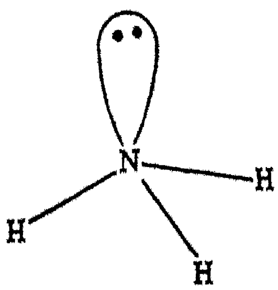
V-shaped
X = 2
P = 1

KX_4



tetrahedral
X = 4

KX_3P



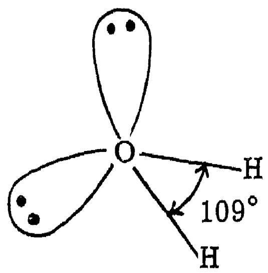
trigonal pyramidal
X = 3
P = 1

Q-16 Illustrate the molecular shape for the following·

a) H_2O b) SF_4 c) I_3^-

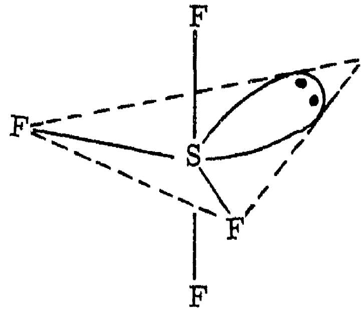
(In I_3^-, place the extra electron on the central I.)

A-16 KX_2P_2



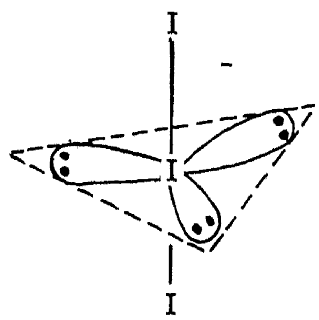
V-shaped
X = 2
P = 2

KX_4P



irregular tetrahedron
X = 4
P = 1

KX_2P_3



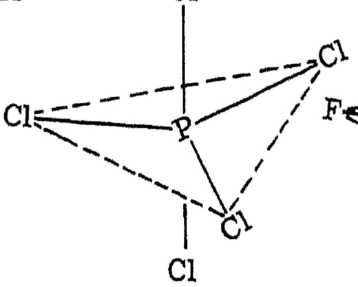
linear
X = 2
P = 3

Q-17 Illustrate the molecular shape for the following compounds

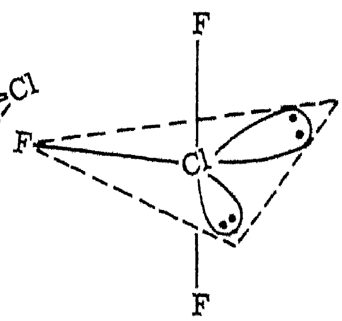
a) PCl_5 b) ClF_3 c) SF_6

In each case the central atom is given first.

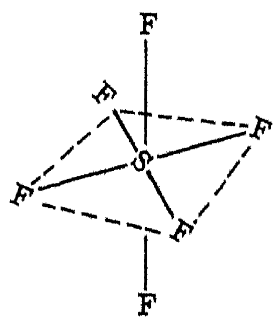
A-17



trigonal bipyramid
X = 5



T-shape
X = 3
P = 2



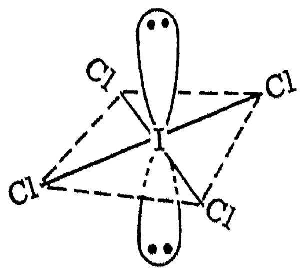
octahedral
X = 6

Q-18 Predict the molecular shape for the following:

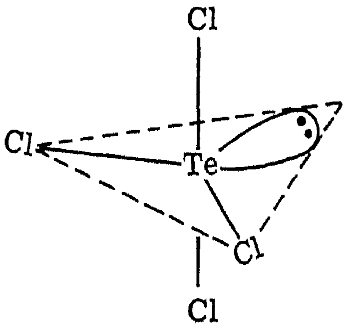
a) $[ICl_4]^-$ b) $TeCl_4$ c) IF_5

In each case the central atom is given first.

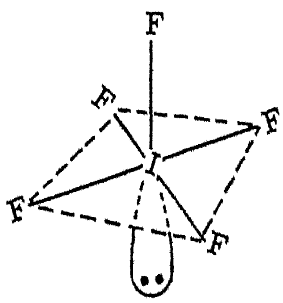
A-18



square planar
X = 4
P = 2



irregular tetrahedron
X = 4
P = 1



square pyramid
X = 5
P = 1

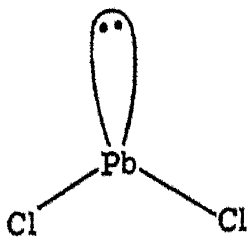
Q-19 Predict the molecular shape for the following

a) $PbCl_2$ b) $SbCl_5$

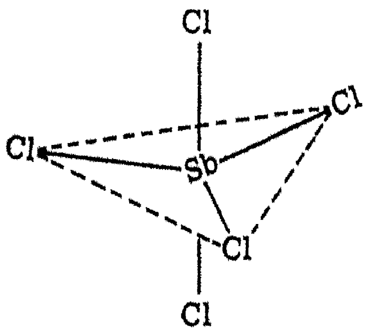
c) $[BF_4^-]$ d) $[SiF_6]^{-2}$

In each case the central atom is given first.

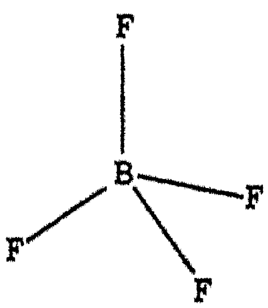
A-19



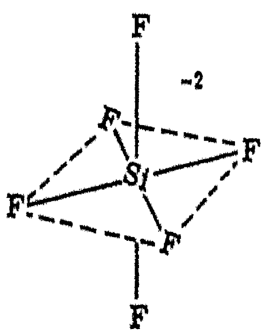
V-shaped
X = 2
P = 1



trigonal bipyramid
X = 5



tetrahedral
X = 4



octahedral
X = 6

R The shape of a molecule can be determined by using the Valence-Shell Electron-Pair Repulsion Theory (VSEPRT). The number of bonding pairs of electrons (X) and non-bonding pairs of electrons (P) are determined. These are arranged around the central atom to minimize repulsion.

PART V: Electronegativity

S-1 Electronegativity is a relative measure of the tendency of a bonded atom to attract electrons to itself In the relative electronegativity scale of Pauling, fluorine is assigned the highest value, 4 0 The other elements are assigned values relative to fluorine The electronegativity values of the elements, given in Table I, will help in predicting whether two atoms will form a covalent or ionic bond

Table I

ELECTRONEGATIVITY VALUES FOR THE ATOMS

H																
2 1																
Li	Be											B	C	N	O	F
1 0	1 5											2 0	2 5	3 0	3 5	4 0
Na	Mg											Al	Si	P	S	Cl
0 9	1 2											1 5	1 8	2 1	2 5	3 0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0 8	1 0	1 3	1 5	1 6	1 6	1 5	1 8	1 8	1 8	1 9	1 6	1 6	1 8	2 0	2 4	2 8
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0 8	1 0	1 2	1 4	1 6	1 8	1 9	2 2	2 2	2 2	1 9	1 7	1 7	1 8	1 9	2 1	2 5
Cs	Ba	La Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0 7	0 9	1 1 1 2	1 3	1 5	1 7	1 9	2 2	2 2	2 2	2 4	1 9	1 8	1 8	1 9	2 0	2 2
Fr	Ra	Ac	Th	Pa	U	Np Lw										
0 7	0 9	1 1	1 3	1 5	1 7	1 3										

Q-1 What trends in the values of the electronegativities are there for elements in the same row of the periodic table?

A-1 Electronegativities increase from left to right across a given row of the periodic table.

Q-2 What trends in the electronegativities are there for elements in the same column of the periodic table?

A-2 Electronegativities increase from bottom to top within a given group (family) of the periodic table.

Q-3 Recalling the trends in ionization energy, what relationship is there between this property and electronegativity?

A-3 The greater the ionization energy, the larger the electronegativity.

Q-4 Does an atom with a high value for the electronegativity have a large or small tendency to attract electrons?

A-4 Large

Q-5 Account for the fact that sodium has a smaller value for electronegativity than chlorine.

A-5 The attraction between a nucleus and electrons will depend upon both the distance between the nucleus and electron and the number of protons in the nucleus. In the Cl atom, the distance from the nucleus to the outermost electrons is less than in the Na atom and the number of protons in the Cl nucleus is greater than that in the Na atom. Therefore, the attraction between the Cl nucleus and electrons in the outermost energy level is much greater than in the case of Na.

Q-6 Account for the fact that Na has a greater electronegativity than K even though K has a higher nuclear charge than Na.

A-6 The electrostatic attraction of the potassium nucleus for its outermost electrons is less than the attraction of the sodium nucleus for its outermost electrons because of the difference in distance from the nucleus to the n = 3 (M) and n = 4 (N) energy levels and the shielding resulting from added electrons. The electrostatic attraction is proportional to the inverse square of the distance and directly proportional to the nuclear charge.

Q-7 If the atoms in a diatomic molecule have identical electronegativities, what can be said about the sharing of the bonding electrons between the two atoms?

A-7 Since the two atoms have an equal tendency to attract electrons, the bonding electrons will be equally shared between the two atoms.

Q-8 If the atoms in a diatomic molecule have different electronegativities, are the electrons shared equally between the two atoms?

A-8 No. The atom with the higher electronegativity will share a greater part of the bonding electrons than the other atom.

Q-9 The unequal sharing of electrons in a bond gives rise to what is called a polar bond. In a polar bond, one atom has a partial negative charge and the other a partial positive charge. In the following diatomic molecules, state which atom has the partial negative charge:

a) H—Cl b) C≡O c) H—H

A-9 a) Cl (higher electronegativity)

b) O (higher electronegativity)

c) neither (electrons are shared equally)

Q-10 The partial positive and negative charges on the atoms in a polar bond give rise to electrostatic interactions. In molecule A—B, the difference in electronegativity between A and B is 1.7. In molecule B—C, the difference in electronegativity between C and B is 1.3. In which molecule are the electrostatic attractions greatest.

A-10 **AB. The greater the difference in the electronegativities between the atoms forming a bond, the greater the electrostatic attractions.**

Q-11 As the electrostatic attractions between atoms increase, the ionic character of the bond increases. How does the ionic character of a bond change as the difference in electronegativity changes?

A-11 The ionic character increases as the difference in electronegativity increases	Q-12 If a bond had 100% ionic character, would the bond be purely ionic or purely covalent?
A-12 Purely ionic	Q-13 If a bond had 0% ionic character, would the bond be purely covalent?
A-13 Yes	Q-14 Between the extremes of pure covalent and pure ionic bonds are bonds with differing degrees of ionic character If the difference in electronegativity of the two elements is 1.7, the bond is said to have 50% ionic character. If the difference in the electronegativities of the two elements is greater than 1.7, what type of bond exists between the two atoms?
A-14 The bond has more ionic character than covalent Therefore, it is called an ionic bond	Q-15 Which of the following compounds is essentially ionic and which is essentially covalent? a) RbCl b NO_2 (Hint: Refer to the Electronegativity table.)
A-15 a) ionic b) covalent	Q-16 Which of the following compounds is essentially covalent and which is essentially ionic? a) BaO b) SO_3
A-16 a) ionic b) covalent	Q-17 Which of the following compounds is essentially ionic and which is essentially covalent? a) IBr b) $SiCl_4$ c) RaO d) KH
A-17 a) covalent b) covalent c) ionic d) covalent	Q-18 Which bond in the following molecules 1) is more polar; 2) has less ionic character; 3) has more covalent bond character? CO NO
A-18 CO more polar NO less ionic character and more covalent bond character	Q-19 Which bond 1) is more polar 2) has less ionic character 3) has more covalent bond character? P—Cl P—I

A-19 P—Cl more polar

P—I less ionic and more covalent bond character

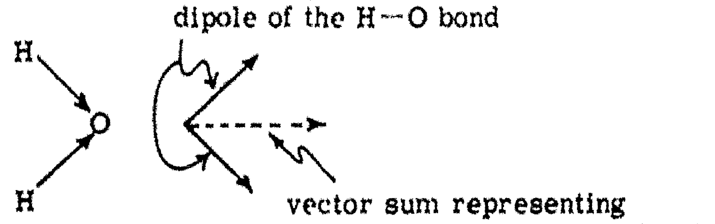
R

a) Electronegativity is a relative measure of the tendency of a bonded atom to attract electrons to itself.

b) A polar bond results when atoms with different electronegativities form a bond.

c) If the electronegativity difference between the bonding atoms is less than 1.7, the bond is considered to be covalent.

S-2 Polar bonds have a positive and an equal negative center separated by a small distance. The Dipole moment of such a bond is given as the charge times the distance between the positive and negative centers. The dipole moment of a molecule is the vectorial sum of the dipoles of all the bonds in the molecule. For example, in H - Cl the dipole of the molecule is equivalent to the dipole of the H—Cl bond. In H_2O the dipole moment of the molecule is the resultant of the dipole moment of the two O—H bonds. The dipole moment vector for the molecule is represented by an arrow pointing in the direction of the negative charge.



Q-20 Which of the following molecules have a dipole moment?

a) H—H b) H—Cl

c) F—F d) F—Br

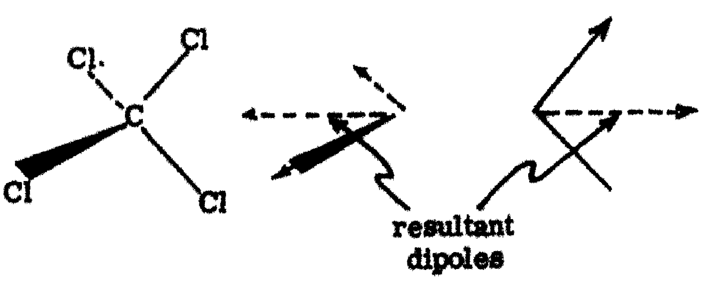
A-20 H—Cl and F—Br have dipole moments.

Q-21 The polar C=O bond has a dipole moment. In CO_2, the O—C—O bond angle is 180°. Explain why CO_2 does not have a dipole moment.

A-21 Since it is a linear molecule, the polar O—C bond in one direction cancels out the effect of the polar C—O bond in the opposite direction.

Q-22 The polar C—Cl bond has a dipole moment yet the molecule CCl_4 does not have a dipole moment. Explain.

A-22 The bond angles in CCl_4 are 109° and the resultant of the dipoles is zero.



Q-23 Which of the following molecules have dipole moments? Why?

a) $BeCl_2$ b) H_2S c) NH_3

A-23 a) no dipole moment (linear)

b) and c) have dipole moments

R **Dipole moment is the resultant of the polarities of all the bonds in a molecule.**

S-3 Bond energy is defined as the energy required to break the bond between two given atoms to form neutral atoms

Q-24 If the bond energy of the Cl—Cl bond is 57.2 kcal/mole and the bond energy of the Br—Br bond is 45.5 kcal/mole, what bond energy would be expected for Br—Cl. Assume that the contribution to bond strength by the Br and Cl atoms is the same as in Cl_2 and Br_2 (equal sharing of electrons).

A-24 $\frac{1}{2}(57.2) + \frac{1}{2}(45.5) = 51.3$ kcal/mole

Q-25 Would the observed bond energy for the Br—Cl bond be greater or less than the value calculated above? Why?

(Hint: Ionic character increases bond strength.)

A-25 Greater - the unequal sharing of electrons gives rise to a polar bond (ionic character) resulting in greater stability

Q-26 If the bond energy of the F—F bond is 38.0 kcal/mole and the bond energy of the I—I bond is 35.5 kcal/mole, what bond energy would be expected for F - I, assuming equal sharing of electrons?

A-26 $\frac{1}{2}(38.0) + \frac{1}{2}(35.5) = 36.7$ kcal/mole

Q-27 Would the observed bond energy be greater or less than the value calculated above? Why?

A-27 Greater - ionic character gives greater stability

Q-28 The calculated and observed bond energies for HCl are 80.2 and 102.1 kcal/mole, respectively, and the calculated and observed bond energies for HBr are 74.3 and 85.9 kcal/mole, respectively. Show how these data indicates that chlorine is more electronegative than bromine.

A-28

HCl (obs.)	102.1	
HCl (calc.)	80.2	
	21.9	difference
HBr (obs.)	85.9	
HBr (calc.)	74.3	
	11.6	difference

The difference between HCl (obs.) and HCl (calc.) is greater than that for HBr. Therefore, the HCl bond has more ionic character, indicating that Cl is more electronegative than Br.

PART VI: Resonance

S-1 The molecule HBr is mainly covalent but it does have some ionic character The Lewis diagram for HBr can be written in a way which will show the ionic character

$$\left[\mathrm{H-\dot{\underset{\cdot\cdot}{Br}}} \longleftrightarrow \mathrm{H^{+}\ _{x}Br^{-}}\right]$$

pure covalent pure ionic

These diagrams are called resonance structures. The actual structure of HBr is said to be a resonance hybrid of the two forms shown above, but lies much closer to the pure covalent structure than to the ionic, since the difference in electronegativities is much less than 1 7. This type of description of a molecule is called resonance.

Q-1 The molecule HCl is mainly covalent but it does have some ionic character. Write the various resonance structures which contribute to the bonding in this molecule.

A-1 $\left[\mathrm{H-\dot{\underset{\cdot\cdot}{Cl}}:} \longleftrightarrow \mathrm{H^{+}\quad {}_{x}^{\cdot}\ddot{\underset{\cdot\cdot}{Cl}}:^{-}}\right]$

pure covalent pure ionic

The actual structure is somewhere in between these two.

Q-2 In the molecule HCl, which resonance structure contributes more to the actual structure?

A-2 $\mathrm{H-\ddot{\underset{\cdot\cdot}{Cl}}:}$

The resonance hybrid of HCl has about 75% covalent and 25% ionic character.

Q-3 Write possible resonance structures for the molecule H_2.

A-3 $\left[\mathrm{H-H} \longleftrightarrow \mathrm{H^{+}\ {}^{\cdot}_{x}H^{-}} \longleftrightarrow \mathrm{H{}^{\cdot}_{x}{}^{-}\ \ H^{+}}\right]$

Q-4 Which resonance structure contributes the most to the actual structure of hydrogen? Why?

A-4 H H

The electronegativities of the two hydrogen atoms are identical, therefore, a pure covalent bond is expected.

Q-5 Write the possible resonance structures for the IBr molecule. Underline the one which contributes more to the resonance hybrid.

A-5 $\left[\underline{\mathrm{:\ddot{\underset{\cdot\cdot}{I}}-\ddot{\underset{\cdot\cdot}{Br}}:}} \longleftrightarrow \mathrm{:\ddot{\underset{\cdot\cdot}{I}}^{+}\quad {}^{x}_{x}\overset{xx}{\underset{xx}{Br}}{}^{x}_{x}{}^{-}}\right]$

Q-6 Why wouldn't the structure

$$\mathrm{:\ddot{\underset{\cdot\cdot}{I}}{}^{\cdot}_{x}{}^{-}\qquad \overset{xx}{\underset{xx}{Br}}{}^{x}_{x}{}^{+}}$$

contribute to the resonance hybrid of the IBr molecule?

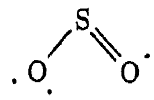
A-6 In this structure the negative charge is on the atom with the lower electronegativity.

Q-7 Write the possible resonance structures for the molecule KH. Underline the structure which contributes more to the resonance hybrid.

A-7 $\left[\underline{K - H} \leftrightarrow K^{+} \quad {}_{x}H^{-}\right]$

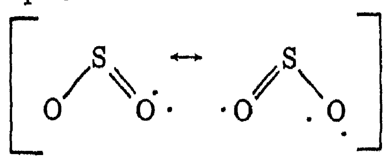
Q-8 Draw a Lewis diagram for SO_2.

A-8



Q-9 The observed bond lengths of the S—O bonds are exactly the same in the SO_2 molecule, and the length is somewhere between a single and double bond length Account for this fact

A-9 This is explained by a resonance description

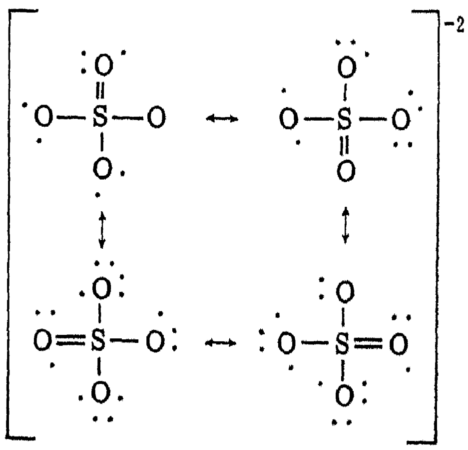


The actual structure of SO_2 is a structure intermediate between these two extremes. The molecule is a <u>resonance hybrid</u> of these two possible contributing structures

Q-10 The sulfate ion, SO_4^{-2}, is found to have four equal S—O bond lengths. Draw Lewis diagrams to account for this observation

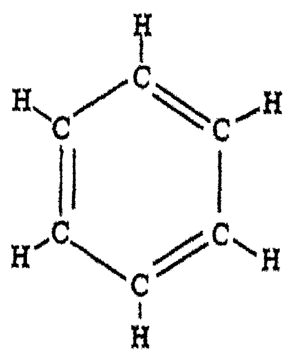
Hint: The S—O bond length is shorter than a single bond. Sulfur can expand its valance shell to accept more than 8 electrons (d orbitals).

A-10



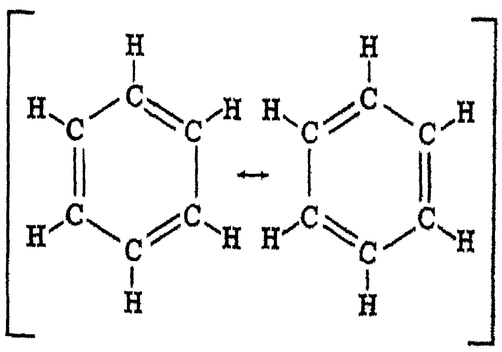
The actual structure is a resonance hybrid of all the above contributing forms.

Q-11 Benzene, C_6H_6, is a molecule with all bond angles 120° and all C—C bond lengths the same. The six carbon atoms form a ring



Account for the equal C—C bond lengths.

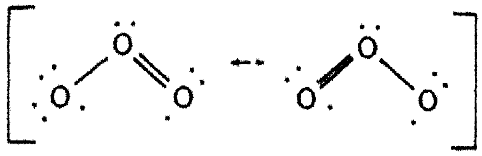
A-11



The actual structure of benzene is considered a resonance hybrid of the two resonance forms shown above.

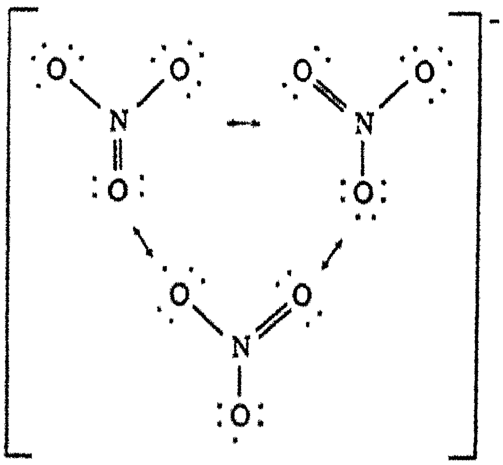
Q-12 The ozone molecule, O_3, has two bonds that are equivalent. Show how resonance can account for this.

A-12



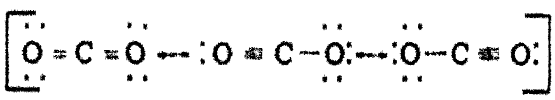
Q-13 The nitrate ion, NO_3^-, contains a central nitrogen atom to which the oxygen atoms are bound The three nitrogen-oxygen bonds are found to be equivalent and at 120° angles Draw electronic formulas for the three contributing resonance forms

A-13



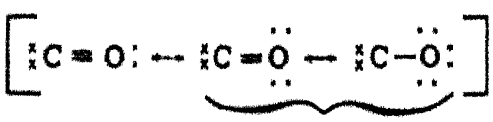
Q-14 Write the three contributing resonance structures for CO_2. The C—O bond distances are equal

A-14



Q-15 The bond distance for carbon monoxide, CO, has been found to be intermediate between a double and triple bond. Draw resonance structures to account for this observation.

A-15



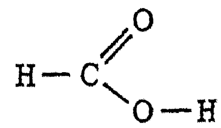
do not contribute very much due to violation of the octet rule

[redacted]

PART VII: Hydrogen Bonding

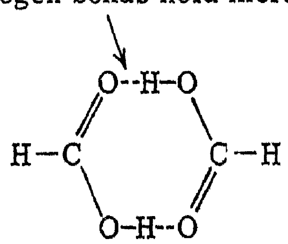
S-1 There are many compounds in which a hydrogen atom exists simultaneously between two atoms, acting as a bridge between them. In this situation the hydrogen atom is involved in two bonds - one is a covalent bond and the other is known as a hydrogen bond. Hydrogen bonds are formed with hydrogens that are covalently bonded to atoms or groups that are highly electronegative (i.e., N—H, O—H, Cl_3C—H, F—H). These hydrogens will form a hydrogen bond with atoms having a high electron density (strongly electronegative atoms such as fluorine, oxygen, and nitrogen). Hydrogen bonds are much weaker than covalent or ionic bonds.

Q-1 Formic acid



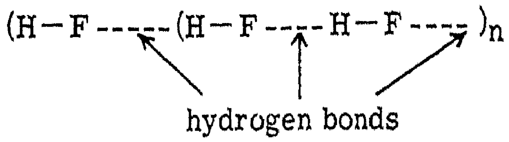
exists as a dimer That is, two molecules of the acid exist as a unit Draw a structure that would account for this dimer formation

A-1 Hydrogen bonds hold molecules together



Q-2 HF is found experimentally to exist as a polymer That is, the HF molecules are linked together in long chains and do not exist as separate units Draw a structure that would account for the polymeric behavior of HF.

A-2

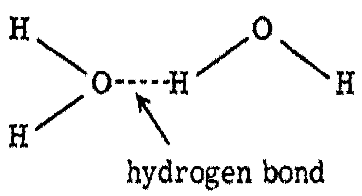


Q-3 The melting points of the group VI binary compounds of hydrogen are as follows.

H_2O	0.0 C
H_2S	- 82.9 C
H_2Se	- 64.0' C
H_2Te	- 51.0' C

Account for the high melting point of H_2O.

A-3 The H_2O molecules are associated together through hydrogen bonds. Therefore, in the H_2O system there are more intermolecular attractions.



The lower electronegativity of S, Se, and Te prevents appreciable hydrogen bond formation in the other molecules.

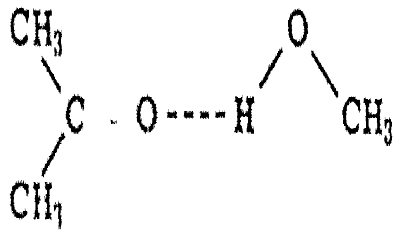
Q-4 The boiling points of the group VII binary compounds of hydrogen are as follows.

HF	19.4' C
HCl	- 83.7 C
HBr	- 67.0' C
HI	- 36.0 C

Account for the high boiling point of HF.

A-4 The HF molecules are associated together through hydrogen bonds. Therefore, more intermolecular attractions between these molecules result in a higher boiling point.

Q-5 Methanol (CH_3OH) forms a hydrogen bond with acetone ($CH_3\overset{\overset{O}{\|}}{C}CH_3$). Diagram the structure of this hydrogen bonded system.

A-5 

Q-6 Chloroform (Cl_3CH) forms a hydrogen bond with trimethylamine,

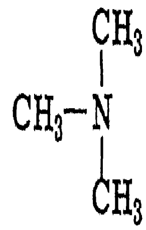
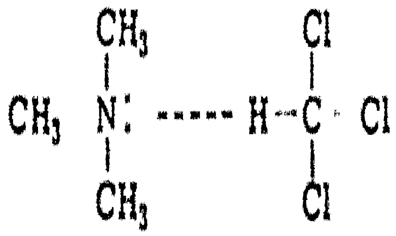
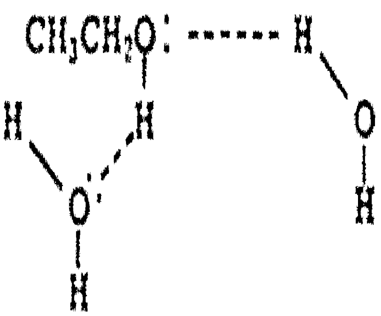


Diagram the structure of this hydrogen bonded system.

A-6 

Q-7 Account for the fact that ethanol (CH_3CH_2OH) is soluble in water while propane ($CH_3CH_2CH_3$) is insoluble in water.

A-7 Ethanol forms hydrogen bonds with water.



The hydrogens of propane cannot form hydrogen bonds because they are not attached to a highly electronegative atom or group.

B Hydrogens covalently bonded to atoms or groups of high electronegativity will hydrogen bond to atoms having high electron density.

NOTES

Chapter 5 | *GASES, LIQUIDS, AND SOLIDS*

Part I <u>Gas Laws</u>

After completing this section you should be able to

a) understand the relationship between the pressure and volume of a gas at constant temperature (Boyle's law)
b) understand the relationship between the temperature and volume of a gas at constant pressure (Charles' law)
c) understand the relationship of the partial pressure of gases to total pressure (Dalton's law)
d) understand the relationship between the volumes of the reactants and products involved in a gaseous reaction (Guy-Lussac's law)
e) understand the relationship between volume and the number of molecules in a given quantity of gas (Avogadro's principle)
f) use the ideal gas equation for calculating pressure, volume and temperature relationships

Part II <u>Kinetic Molecular Theory</u>

After completing this section you should understand

a) the properties of an ideal gas
b) the kinetic molecular theory interpretation of the gas laws
c) the effect of a temperature change upon the distribution of energy in a gas sample
d) why real gases deviate from ideal behavior

Part III <u>Liquids</u>

After completing this section you should understand

a) why gases condense to liquids and why liquids evaporate
b) the dependence of vapor pressure on temperature
c) the relationship between vapor pressure and boiling point

Part IV· <u>Solids</u>

After completing this section you should

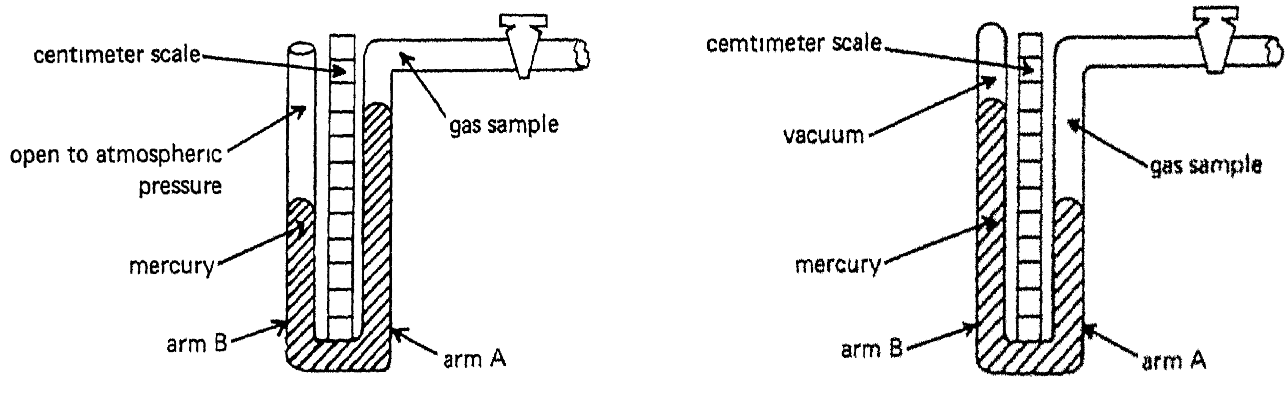
a) understand the relationship between the structure of solids and their physical properties
b) understand why liquids freeze, and what is meant by the melting point of a solid
c) understand the geometrical arrangement of simple crystals
d) be able to calculate the size of the unit cell, atomic weight, and Avogadro's number, given certain information about a crystal

PART I: Gas Laws

S-1 All gases

a) can be easily compressed into a small volume
b) will expand to fill the vessel containing them
c) will exert pressure equally in all directions.

Gas pressure can be measured with open or closed end manometers. These devices are illustrated below



Open-end Manometer   Closed-end Manometer

Q-1 The pressure of a gas measured with a closed end manometer is reported as the <u>difference</u> between the mercury levels in the two arms of the manometer. If the height of mercury in arm A of the manometer is 200 mm and the mercury heighth in arm B is 950mm, what is the pressure of the gas sample in mm of Hg?

A-1 (950 - 200) mm Hg = 750 mm Hg.

Q-2 Another pressure unit frequently used is the torr. The torr is equal to 1 mm Hg. If the one arm of a closed-end manometer reads 120.0 cm and the other arm reads 75.0 cm, what is the pressure reading of the manometer in cm of Hg, mm of Hg, and torr?

A-2 120.0 - 75.0 = 45.0 cm of Hg

$$\frac{45.0\ \cancel{cm}\text{ of Hg}}{} \left|\frac{10\text{mm}}{1\ \cancel{cm}}\right. = 450\text{ mm of Hg}$$

$$\frac{450\ \cancel{\text{mm of Hg}}}{} \left|\frac{1\text{ torr}}{1\ \cancel{\text{mm of Hg}}}\right. = 450\text{ torr}$$

Q-3 In the open-end manometer, the pressure of a gas sample is obtained by subtracting the difference between the Hg levels in the two arms of the manometer from atmospheric pressure.

If atmospheric pressure is 74.0 cm Hg, and the height of the mercury in arm A is 84.5 cm and the height of the mercury in arm B is 24.3 cm, what is the pressure of the gas sample in cm of Hg.

A-3 74 0 cm of Hg - (84 5 cm Hg - 24 3 cm Hg) = 13 8 cm Hg

Q-4 The pressure of a gas sample was measured with both a closed-end and an open-end manometer and found to be 32 5 cm of Hg If atmospheric pressure was 74 5 cm of Hg, what was the difference in height between the Hg levels in each manometer when the measurements were made?

A-4 Closed-end 32 5 cm

Open-end. 74 5 - (difference in height) = 32 5

Difference in height = 74 5 - 32 5

= 42 0

Q-5 Gas pressures are also expressed in terms of a quantity called atmospheres.

1 atm = 76 0 cm of Hg

If one arm of a closed-end manometer reads 273 mm and the other arm reads 122 mm, what is the pressure reading of the manometer in atmospheres?

A-5 273 - 122 = 151 mm of Hg

$$\frac{151\ \cancel{\text{mm of Hg}}}{} \left| \frac{1\ \cancel{\text{cm}}}{10\ \cancel{\text{mm}}} \right| \frac{1\ \text{atm}}{76\ 0\ \cancel{\text{cm}}}$$

pressure = 0 199 atm

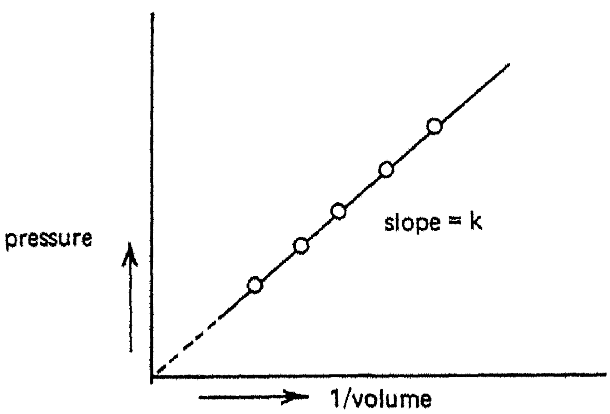
Q-6 What is the pressure in atm if the difference in the levels of Hg in an open-end manometer is 70 cm? 500 mm? (Atmospheric pressure = 74 0 cm)

A-6 $\dfrac{4\ 0\ \cancel{\text{cm}}}{} \left| \dfrac{1\ \text{atm}}{76\ \cancel{\text{cm}}} \right. = 0\ 053$ atm

$\dfrac{240\ \cancel{\text{mm}}}{} \left| \dfrac{1\ \text{atm}}{760\ \cancel{\text{mm}}} \right. = 0\ 316$ atm

[redacted]

S-2 Robert Boyle found that a linear relationship exists between the pressure (P) and the reciprocal of the volume (1/V) for a given amount of gas at constant temperature He constructed graphs similar to the following



Q-7 Give a mathematical expression for the relationship between P and V. (Hint: The equation for a straight line is y = ax + b)

A-7 From the plot of P vs 1/V, it is seen that y = P and x = 1/V. The y intercept (b) is equal to zero. The slope (a) is equal to k. Therefore, the equation is

$P = (k)(1/V)$ or

$PV = k$ (a constant)

This is known as Boyle's law

Q-8 A given amount of gas at 25°C occupies a volume of 150 ml at a pressure of 700 mm of Hg. What would be the volume of the gas if the pressure were increased to 1050 mm of Hg keeping the temperature constant? (Hint: Consider the equation for the gas in the original state and the final state.)

A-8 $P_1V_1 = k$

$P_2V_2 = k$ Therefore,

$P_1V_1 = P_2V_2$

$P_1 = 700$ mm $V_1 = 150$ ml

$P_2 = 1050$ mm $V_2 = ?$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{(700\ \cancel{mm})(150\ ml)}{1050\ \cancel{mm}} = 100\ ml$$

Q-9 A gas is expanded, at constant temperature, from a volume of 400 ml to a volume of 1 liter, where its final pressure is 100 mm of Hg. What was the original pressure?

(1 liter = 1000 ml)

A-9 $P_1V_1 = P_2V_2$

$P_1 = ?$ $V_1 = 400$ ml

$P_2 = 100$ mm $V_2 = \dfrac{1\ \cancel{liter}}{} \Big| \dfrac{1000\ ml}{1\ \cancel{liter}}$

$= 1000$ ml

$$P_1 = \frac{P_2V_2}{V_1} = \frac{(100\ mm)(1000\ \cancel{ml})}{(400\ \cancel{ml})}$$

$P_1 = 250$ mm of Hg

Q-10 A 2.0g sample of a gas occupies 8.4 liters at 0°C and 760 mm of Hg. Calculate the volume at 0°C and a pressure of 84 cm of Hg?

A-10 $V_1P_1 = V_2P_2$

$V_1 = 8.4$ liter $P_1 = 760$ mm

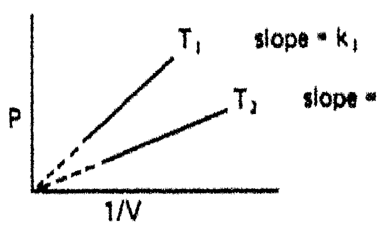
$V_2 = ?$ $P_2 = \dfrac{84\ \cancel{cm}}{} \Big| \dfrac{10\ mm}{1\ \cancel{cm}}$

$= 840$ mm

$$V_2 = \frac{V_1P_1}{P_2} = \frac{(8.4\ liter)(760\ \cancel{mm})}{840\ \cancel{mm}}$$

$V_2 = 7.6$ liter

Q-11 For a given amount of gas, a plot of P vs 1/V at two different temperatures is shown below.

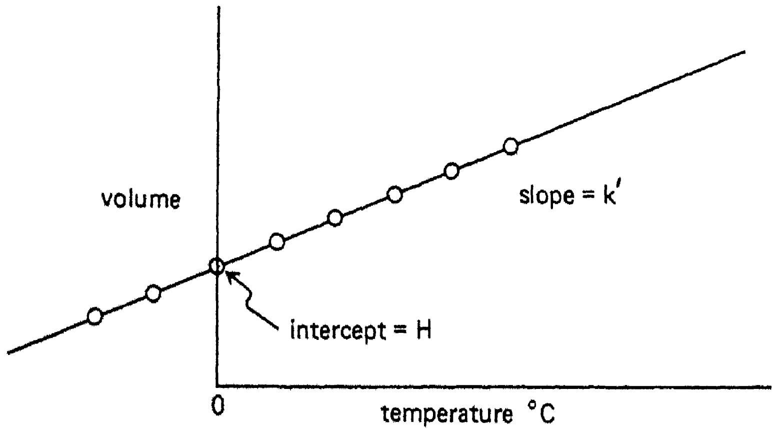


Why can't the equation $P_1V_1 = P_2V_2$ be used if the temperature changes?

A-11 Boyle's law states that PV = k, where k is the slope of the line. For two sets of pressure-volume conditions the slopes k_1 and k_2 are equated to give $P_1V_1 = P_2V_2$. However, if the temperature changes, the slopes (k_1 and k_2) are different and cannot be set equal to one another

[redacted]

S-3 For a given amount of gas at a constant pressure, Jacques Charles found the following relationship between volume (V) and temperature (t)



Q-12 Give a mathematical expression for the relationship between V and t H has been determined experimentally to be equal to (273) k' and this value should be substituted for H in the derivation

A-12 Equation of a straight line

$$y = ax + b$$

$V = k'(t) + H$

$V = k'(t) + k'(273°)$

$V = k'(t + 273°)$

(k' is not the same constant as the k from Boyle's law)

Q-13 A new temperature scale is defined where $T = t°C + 273°$. T is called the absolute temperature and is expressed in degrees Kelvin (°K). Therefore, at constant pressure

$V = k'T$ or $\frac{V}{T} = k'$

Is V inversely or directly proportional to T?

A-13 V is directly proportional to T.

Q-14 Is V inversely or directly proportional to P? (Hint Boyle's law, $PV = k$)

A-14 V is inversely proportional to P

Q-15 What is the freezing point of water on the absolute temperature scale?

A-15 freezing point = 0°C

$T = 0°C + 273° = 273°K$

Q-16 What is the boiling point of water on the absolute temperature scale?

A-16 boiling point of H_2O = 100°C

$T = 100°C + 273° = 373°K$

Q-17 A given amount of gas at one atm pressure was heated from 0°C to 100°C. If the initial volume were 1.0 liter, what would be the final volume if the pressure remained constant?

A-17 $\frac{V_1}{T_1} = k'$ and $\frac{V_2}{T_2} = k'$ Therefore,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 1.0$ liter $\quad V_2 = \ ?$

$T_1 = 273\,°K \quad T_2 = 373\,°K$

$$V_2 = \frac{V_1T_2}{T_1} = \frac{(1.0 \text{ liter})\,(373\,°\cancel{K})}{273\,°\cancel{K}}$$

$= 1.4$ liter

Q-18 A 2.0 g sample of gas occupies 8.4 liters at 20°C and 1 atm pressure. What is its volume at 91°C and a pressure of 76 cm Hg?

A-18 Since the pressure remains constant,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 8.4$ liter $\quad V_2 = \ ?$

$T_1 = 293\,°K \quad T_2 = 364\,°K$

$$V_2 = \frac{V_1T_2}{T_1} = \frac{(8.4 \text{ liter})\,(364\,°\cancel{K})}{293\,°\cancel{K}}$$

$= 10$ liter

Q-19 A sample of nitrogen gas weighing 9.3 g at a pressure of 75.0 cm Hg occupies a volume of 12.3 liters when its temperature is 450°K. What is its volume at a temperature of 125°C, and a pressure of 75.0 cm of Hg?

A-19 Since the pressure remains constant,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 12.3$ liter $\quad V_2 = \ ?$

$T_1 = 450°K \quad T_2 = 125 + 273$

$= 398°K$

$$V_2 = \frac{V_1T_2}{T_1} = \frac{(12.3 \text{ liter})\,(398\,°\cancel{K})}{450°\,\cancel{K}}$$

$= 10.9$ liter

R Boyle's law:

$PV = k$ at constant T

Charles' law:

$\frac{V}{T} = k'$ at constant P

S-4 The customary reference point for gases is at 273°K (0°C) and 1 standard atmosphere (760 mm of Hg) pressure. These standard conditions are called <u>standard temperature and pressure</u> (STP).

Q-20 A given quantity of gas at 760 mm of Hg and a temperature of 25°C occupies a volume of 2.0 liters. What is the volume of the same amount of gas at STP?

A-20 The original and final pressures are identical. Therefore,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$V_1 = 2.0$ liter $\quad V_2 = \ ?$

$T_1 = 298°K \quad T_2 = 273°K$

$$V_2 = \frac{V_1T_2}{V_1} = \frac{(2.0 \text{ liter})\,(273\,°\cancel{K})}{298\,°\cancel{K}}$$

$= 1.8$ liter

Q-21 At STP a given quantity of gas occupies 5.00 liters. What is the temperature of this same quantity of gas at the same pressure when it occupies a volume of 10.0 liters?

A-21 $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$V_1 = 5.0$ liter $V_2 = 10.0$ liter

$T_1 = 273$ K $T_2 = \ ?$

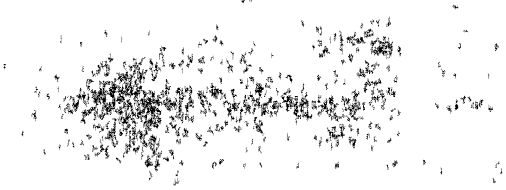
$$T_2 = \frac{V_2T_1}{V_1} = \frac{(10.0\ \cancel{\text{liter}})(273\,^\circ\text{K})}{5.00\ \cancel{\text{liter}}}$$

$= 546\,^\circ$K

R **Standard conditions for gases:**

T = 273°K (0°C)

P = 760 mm Hg



S-5 John Dalton observed that when two or more gases are placed in the same container, the total pressure exerted by the mixture of gases is equal to the sum of the partial pressures of the various gases. The partial pressure is the pressure the gas would exert if it were alone in the container.

Q-22 Two gases, A and B, when placed in a container gave a total pressure reading of 823 mm of Hg. The pressure of A alone in the container was known to be 456 mm of Hg. What is the pressure of gas B in the container?

A-22 823 mm Hg A + B
-456 mm Hg A
367 mm Hg B

Q-23 The partial pressures of H_2, O_2, and N_2 in a container are 350 mm of Hg, 26.0 cm of Hg, and 0.50 atm, respectively. What is the total pressure in the container?

A-23 $\frac{26\ \cancel{\text{cm Hg}} \mid 10\ \text{mm Hg}}{\mid 1\ \cancel{\text{cm Hg}}} = 260$ mm Hg

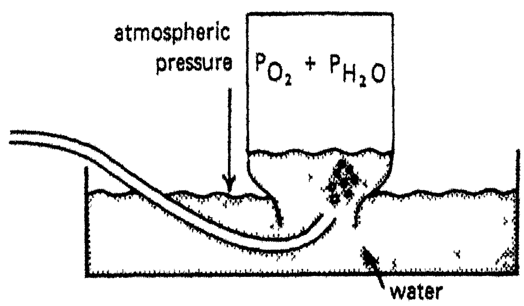
$\frac{0.5\ \cancel{\text{atm Hg}} \mid 760\ \text{mm Hg}}{\mid 1\ \cancel{\text{atm Hg}}} = 380$ mm Hg

350 mm of Hg H_2
260 mm of Hg O_2
380 mm of Hg N_2
990 mm of Hg Total pressure in in container.

Q-24 In laboratory experiments gases are often collected above water, and water vapor contributes to the total pressure measured. If, in a collecting bottle, the measured pressure is 740.0 mm of Hg at 21°C, what would be the pressure of the gas collected? (vapor pressure of water at 21°C = 18.7 mm of Hg)

A-24 740.0 total pressure
-18.7 pressure of water vapor
721.3 mm of Hg (pressure of collected gas)

Q-25 The equipment used for collecting O_2 was arranged in the following manner:



The pressure inside was obtained by adjusting the water inside the bottle to the height of the water outside of the bottle. When this adjustment was made, what was the pressure inside the bottle?

A-25 If the water levels inside and outside were the same, the pressure inside the bottle would be equal to the atmospheric pressure

Q-26 The apparatus in Q-25 was used to collect 4 0 liter of O_2 at a temperature of 25°C What would be the volume of dry O_2 at 1 atm pressure and the same temperature? The atmospheric pressure for the experiment was 750 0 mm Hg, the vapor pressure of water at 25°C is 23 8 mm Hg

A-26 $V_1P_1 = V_2P_2$

$V_1 = 4\ 0$ liter

$V_2 = ?$

$P_1 = (750\ 0 - 23\ 8)$ mm Hg

$= 726.2$ mm Hg

$$P_1 = \frac{726\ 2\ \cancel{\text{mm Hg}}}{} \bigg| \frac{1\ \text{atm}}{760\ 0\ \cancel{\text{mm Hg}}} =$$

$= 0\ 956$ atm

$$V_2 = \frac{V_1P_1}{P_2} = \frac{(4.0\ \text{liter})(0\ 956\ \cancel{\text{atm}})}{1.0\ \cancel{\text{atm}}}$$

$= 3\ 8$ liter

R **Dalton's law**

$$P_{total} = P_A + P_B \ldots + P_N$$

S-6 Gay-Lussac found that there was a definite relationship between the volumes of gases involved in chemical reactions. Through experimental observations, he arrived at his law of combining volumes which states: whenever two or more gases are involved in a chemical reaction, the ratios of the volumes of the gases may be expressed as the ratios of small integral numbers, provided the volumes are measured at the same temperature and pressure.

Q-27 Show how the following data illustrates the law of Gay-Lussac.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

	Volume of gas reacted or produced at 100°C and 1 atm pressure
H_2	0.336 liters
O_2	0.168 liters
H_2O	0.336 liters

A-27 $\frac{\text{volume of } H_2}{\text{volume of } O_2}\ \frac{0\ 336}{0.168} = \frac{2}{1}$

$\frac{\text{volume of } H_2}{\text{volume of } H_2O}\ \frac{0\ 336}{0.336} = \frac{1}{1}$

$\frac{\text{volume of } O_2}{\text{volume of } H_2O}\ \frac{0.168}{0\ 336} = \frac{1}{2}$

Q-28 In the reaction $H_2 + Cl_2 \rightarrow 2HCl$, what volume of Cl_2 would Gay-Lussac have observed to react with 1 liter of H_2?

A-28 $\frac{\text{volume of } H_2}{\text{volume of } Cl_2} = \frac{1}{1}$

1 liter of Cl_2

Q-29 What are the volume relationships for the gases reacting and being formed in the reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

A-29 If all gases involved are measured at the same pressure and temperature, one unit volume of methane (CH_4) would react with two unit volumes of oxygen to produce one unit volume of carbon dioxide (CO_2) and two unit volumes of water vapor.

Q-30 In the reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

how many liters of oxygen are necessary to react with 100 liters of methane? How many liters of CO_2 and steam are produced? (Assume all reactants and products are measured at the same pressure and temperature.)

A-30 $\dfrac{100\ \cancel{\text{liter } CH_4}}{} \Big| \dfrac{2\ \text{liter } O_2}{1\ \cancel{\text{liter } CH_4}}$

$= 200$ liter O_2

$\dfrac{100\ \cancel{\text{liter } CH_4}}{} \Big| \dfrac{1\ \text{liter } CO_2}{1\ \cancel{\text{liter } CH_4}}$

100 liter CO_2

$\dfrac{100\ \cancel{\text{liter } CH_4}}{} \Big| \dfrac{2\ \text{liter } H_2O}{1\ \cancel{\text{liter } CH_4}}$

200 liter H_2O

Q-31 A hypothetical chemical equation that represents a reaction involving gases is

$$2X_2Y_3 + 5Z_2 \rightarrow 3Z_3Y_2 + ZX_4$$

(All gases remain at the same pressure and temperature.)

What is the maximum volume, in milliliters, of Z_3Y_2 that would be obtained from a reaction initiated by mixing 30 ml of X_2Y_3 and 100 ml of Z_2?

(Hint: Determine if any reactants are present in excess.)

A-31 Given 30 ml of X_2Y_3,

then $\dfrac{30\ \cancel{\text{ml } X_2Y_3}}{} \Big| \dfrac{5\ \text{ml } Z_2}{2\ \cancel{\text{ml } X_2Y_3}}$

= 75 ml Z_2 needed to react completely with X_2Y_3

Since the initial volume of Z_2 was 100 ml, Z_2 is present in excess. Therefore, X_2Y_3 determines the amount of products formed.

$\dfrac{30\ \cancel{\text{ml } X_2Y_3}}{} \Big| \dfrac{3\ \text{ml } Z_3Y_2}{2\ \cancel{\text{ml } X_2Y_3}} = 45$ ml Z_3Y_2

Q-32 In the reaction of Q-31, how many ml of Z_2 are needed to react completely with 25 ml of X_2Y_3?

A-32 $\dfrac{25\ \cancel{\text{ml } X_2Y_3}}{} \Big| \dfrac{5\ \text{ml } Z_2}{2\ \cancel{\text{ml } X_2Y_3}} = 62$ ml Z_2

Q-33 If 50 ml of X_2Y_3 reacts completely with 200 ml of Z_2 in a closed vessel, what mixture of gases will result?

$$2X_2Y_3 + 5Z_2 \rightarrow 3Z_3Y_2 + ZX_4$$

A-33 Amount of Z_2 reacted

$$\frac{50\ \cancel{ml\ X_2Y_3}}{} \bigg| \frac{5\ ml\ Z_2}{2\ \cancel{ml\ X_2Y_3}} = 125\ ml\ Z_2$$

Therefore, the vessel would contain unreacted Z_2 and the products Z_3Y_2 and ZX_4

Z_2 = 200 ml (initial) - 125 ml (reacted)

= 75 ml Z_2 remaining

$$Z_3Y_2 = \frac{50\ \cancel{ml\ X_2Y_3}}{} \bigg| \frac{3\ ml\ Z_3Y_2}{2\ \cancel{ml\ X_2Y_3}}$$

= 75 ml Z_3Y_2

$$ZX_4 = \frac{50\ \cancel{ml\ X_2Y_3}}{} \bigg| \frac{1\ ml\ ZX_4}{2\ \cancel{ml\ X_2Y_3}}$$

= 25 ml ZX_4

Q-34 In a chemical reaction such as

$$H_2 + Cl_2 \rightarrow 2HCl$$

one molecule of H_2 reacts with one molecule of Cl_2 to produce 2 molecules of HCl Considering Gay-Lussac's law of combining volumes, what can be said about the number of molecules present in equal volumes of different gases at identical pressure and temperature?

A-34 Gay-Lussac's law states that one volume of H_2 reacts with one volume of Cl_2 Since one molecule of H_2 reacts with one molecule of Cl_2, equal volumes of H_2 and Cl_2 must contain the same number of molecules

Q-35 The principle derived in A-34 was first given by Avogadro. Avogadro's principle states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

What is the mathematical relationship between volume and number of molecules (n) at constant temperature and pressure?

A-35 The volume is proportional to the number of molecules (n).

$V \propto n$ (constant P and T)

$V = k''n$ (where k'' is a proportionality constant)

$$\frac{V}{n} = k''$$

Q-36 If the number of moles of gas were doubled and the pressure and temperature remained the same, what would happen to the volume?

A-36 Volume is doubled.

Q-37 The volume occupied at STP by 1 mole of oxygen has been determined by experiment to be 22.4 liters. This is called the molar volume of oxygen at STP. What is the molar volume of H_2 at STP?

A-37 Since 1 mole of gas contains an Avogadro number of molecules, and at the same temperature and pressure the same number of molecules of different gases occupies the same volume, one mole of H_2 at STP would occupy 22.4 liters.

Q-38 At STP 1 liter of H_2 and 1 liter of O_2 are observed to weigh 0.0900 g and 1.43 g respectively. Given that the molecular weight of O_2 is 32, what is the molecular weight of H_2?

A-38 Since the number of molecules is the same in each sample, each hydrogen molecule must be

$\frac{0.0900}{1.43}$ times as heavy as each oxygen molecule

$$\text{MW of } H_2 = \frac{0.0900 \text{ g } H_2}{1 \cancel{\text{liter}}} \left| \frac{1 \cancel{\text{liter}}}{1.43 \cancel{\text{g } O_2}} \right| \frac{32 \cancel{\text{g } O_2}}{1 \text{ mole}} = 2.0 \text{ g/mole}$$

Q-39 At STP 1.00 liter of chlorine (Cl_2) is observed to weigh 3.16 g, and 1.00 liter of hydrogen (H_2) 0.0900 g. Given that the molecular weight of H_2 is 2.00, what is the molecular weight of Cl_2?

A-39 $$\text{MW of } Cl_2 = \frac{3.16 \text{ g } Cl_2}{1.00 \cancel{\text{liter}}} \left| \frac{1.00 \cancel{\text{liter}}}{0.0900 \cancel{\text{g } H_2}} \right| \frac{2.00 \cancel{\text{g } H_2}}{1 \text{ mole}} = 70.2 \text{ g/mole}$$

Q-40 The density of a gas at STP is 1.40 g per liter. What is the molecular weight of the gas? (Hint: One mole of gas at STP occupies 22.4 ℓ.)

A-40 $$\text{MW} = \frac{1.40 \text{ g}}{1 \cancel{\text{liter}}} \left| \frac{22.4 \cancel{\text{liter}}}{1 \text{ mole}} \right.$$

$= 31.4$ g/mole

Q-41 Chemical analysis shows that the empirical formula of ethylene is CH_2. Ethylene has a density of 1.25 g per liter at STP. What is the molecular weight and the molecular formula of ethylene?

A-41 $$\text{MW} = \frac{1.25 \text{ g}}{1 \cancel{\text{liter}}} \left| \frac{22.4 \cancel{\text{liter}}}{1 \text{ mole of gas}} \right.$$

$= 28.0$ g/mole

The empirical weight is

$$\begin{aligned} C &= 12.0 \\ 2H &= \underline{\ \ 2.0} \\ &\ \ \ 14.0 \end{aligned}$$

The molecular formula is some multiple of CH_2, i.e., $(CH_2)_x$.

Since the molecular weight is a multiple of the empirical weight,

$$x = \frac{28}{14} = 2$$

and

molecular formula $= (CH_2)_2 = C_2H_4$

Q-42 What is the volume occupied by 4.0 grams of ethylene at STP?

A-42. $$\frac{4.0 \cancel{\text{g ethylene}}}{} \left| \frac{1 \cancel{\text{mole ethylene}}}{28 \cancel{\text{g ethylene}}} \right| \frac{22.4 \text{ liter STP}}{1 \cancel{\text{mole ethylene}}} = 3.2 \text{ liter at STP}$$

Q-43 How many molecules are there in 6.0 liters of CO_2 at STP?

A-43 Remembering that one mole = 6 023 x 10^{23} molecules,

$$\frac{6\ 0\ \cancel{\text{liter}}}{} \left| \frac{1\ \cancel{\text{mole}}}{22\ 4\ \cancel{\text{liter}}} \right| \frac{6\ 023 \times 10^{23}\ \text{molecules}}{1\ \cancel{\text{mole}}} = 1\ 6 \times 10^{23}\ \text{molecules}$$

Q-44 How many grams of gas at 1 atm and 273°K occupy 3 00 liters if, under these conditions, the density of the gas is 4 48 g/liter? What is the molecular weight of the gas?

A-44 $\frac{3\ 00\ \cancel{\text{liter}}}{} \left| \frac{4\ 48\ g}{1\ \cancel{\text{liter}}} \right. = 13\ 4\ g$

$MW = \frac{4\ 48\ g}{1\ \cancel{\text{liter}}} \left| \frac{22\ 4\ \cancel{\text{liter}}}{1\ \text{mole}} \right. = 100\ g/\text{mole}$

Q-45 A 0°C and 2 0 atm, the density of a gas is 2 5 g/liter. What is the density of the gas at standard conditions?

A-45 $V_1P_1 = V_2P_2$

$V_1 = 1\ 0$ liter $V_2 = \ ?$

$P_1 = 2.0$ atm $P_2 = 1\ 0$ atm

$V_2 = \frac{V_1P_1}{P_2} = \frac{(1\ 0\ \text{liter})(2\ 0\ \text{atm})}{1\ 0\ \text{atm}}$

$= 2\ 0$ liter at STP

$d = \frac{2\ 5\ g}{2\ 0\ \text{liter}} = \frac{1\ 2\ g}{\text{liter}}$

Q-46 What is the mass of 1 25 moles of gas if its density is 1 50 g/liter at 273°K and 380 mm of Hg? (Hint Find the density at STP first.)

A-46 $P_1V_1 = P_2V_2$

$P_1 = 380$ mm $P_2 = 760$ mm

$V_1 = 1\ 00$ liter $V_2 = \ ?$

$V_2 = \frac{P_1V_1}{P_2} = \frac{(380\ \cancel{\text{mm}})(1\ 00\ \text{liter})}{760\ \cancel{\text{mm}}} = 0.500$ liter (at STP)

The density at STP is

1 50 g/0 500 liter = 3.00 g/liter

$\text{mass} = \frac{3.00\ g}{1\ 00\ \cancel{\text{liter}}} \left| \frac{22.4\ \cancel{\text{liter}}}{1\ \cancel{\text{mole}}} \right| \frac{1.25\ \cancel{\text{mole}}}{} = 84.0\ g$

Q-47 Given that $X \alpha Y$ and $X \alpha \frac{1}{Z}$, combine the two proportionality expressions into one expression.

A-47 $X \alpha Y$ $X \alpha \frac{1}{Z}$

Therefore, $X \alpha (Y) (\frac{1}{Z})$

Q-48 Write the proportionality expression of A-47 in equation form.

A-48 $X = A (Y) (\frac{1}{Z})$

A is a proportionality constant.

Q-49 X is found to be directly proportional to a third quantity (W). Write an equation relating X to the quantities Y, Z and W.

A-49 $X \alpha (Y) (\frac{1}{Z})$ $X \alpha W$

Combining the above expressions give

$$X \alpha (Y) (\frac{1}{Z}) (W)$$

$$X = B (Y) (\frac{1}{Z}) (W)$$

B is a proportionality constant

Q-50 Using the equations given for Boyle's law, ($V \alpha 1/P$), Charles' law, ($V \alpha T$) and Avegadre's principle ($V \alpha n$) derive an equation which will relate P, V, T, and n to each other An equation which gives the relationship between the volume, pressure, temperature and number of moles of a gas is called an equation of state

A-50 Boyle's law

$V \alpha \frac{1}{P}$ constant T and n

Charles' law

$V \alpha T$ at constant P and n

Avogadro's principle

$V \alpha n$ at constant T and P

$V \alpha (\frac{1}{P}) (T) (n)$ or $V = R (\frac{1}{P}) (T) (n)$

where R is a proportionality constant. n, the number of molecules, is expressed in terms of moles. This equation of state is called the ideal gas equation.

Q-51 Using the ideal gas equation derive an expression for k of Boyle's law in terms of R, T, and n

A-51 $V = \frac{k}{P}$ or $VP = k$

The ideal gas equation gives $VP = RTn$. Therefore, $k = RTn$

Q-52 Using the ideal gas equation, derive an expression for k' of Charles' law in terms of R, n, and P.

A-52 $V = k'T$ or $\frac{V}{T} = k'$

$$\frac{V}{T} = \frac{Rn}{P}$$

Therefore, $k' = \frac{Rn}{P}$

Q-53 Evaluate the constant, R, in the ideal gas equation. Use standard condition values for V, P, and T, for one mole of gas ($n = 1$) in the following units:

V (liters), P (atm), T (°Kelvin)

A-53 $\frac{VP}{Tn} = R$

V = 22.4 liter P = 1 atm

T = 273 °K n = 1 mole

$$\frac{(22.4 \text{ liter}) (1 \text{atm})}{(273\,^\circ\text{K}) (1 \text{ mole})} = 0.0820 \text{ liter-atm/mole-deg}$$

Q-54 What would the constant R be in units of cc-mm of Hg per mole-deg?

A-54 $\frac{0.0820\ \cancel{\text{liter-atm}}}{\text{mole-deg}} \left| \frac{1000\ \text{cc}}{1\ \cancel{\text{liter}}} \right| \frac{760\ \text{mm Hg}}{1\ \cancel{\text{atm}}} = 6.23 \times 10^4 \frac{\text{cc-mm Hg}}{\text{mole-deg}}$

Q-55 A 7.0 g sample of N_2 occupies 8.4 liters at a temperature of 20°C. What is the pressure of the sample under these conditions? (Hint: Use the ideal gas equation.)

A-55 PV = nRT

P = ?

V = 8.4 liter

R = 0.082 liter-atm/mole-deg

T = 273 + 20 = 293°K

$n = \frac{7.0\ \cancel{g\ N_2}}{} \left| \frac{1\ \text{mole}}{28\ \cancel{g\ N_2}} \right. = 0.25\ \text{moles}$

$P = \frac{(0.25\ \cancel{\text{mole}})\ (293\ \cancel{°K})\ (0.082\ \cancel{\text{liter}}\text{-atm})}{8.4\ \cancel{\text{liter}}\qquad \cancel{\text{deg-mole}}} = 0.71\ \text{atm}$

Q-56 A 5.0 g sample of oxygen (O_2) occupies 4.0 liters at a pressure of 473 mm of Hg. What is the temperature of the O_2 under these conditions?

A-56 PV = nRT

$P = \frac{473\ \cancel{\text{mm Hg}}}{} \left| \frac{1\ \text{atm}}{760\ \cancel{\text{mm Hg}}} \right. = 0.622\ \text{atm}$

V = 4.0 liters

R = 0.082 liter-atm/mole-deg

T = ?

$n = \frac{5.0\ \cancel{g\ O_2}}{} \left| \frac{1\ \text{mole}}{32\ \cancel{g\ O_2}} \right. = 0.16\ \text{moles}$

$T = \frac{(0.622\ \cancel{\text{atm}})\ (4.0\ \cancel{\text{liter}})\ (\cancel{\text{mole}}\text{-deg})}{(0.16\ \cancel{\text{mole}})\quad (0.082\ \cancel{\text{liter-atm}})} = 190°K$

Q-57 Find the number of moles of a gas that would occupy 10.2 liters at a pressure of 3.7 atm and a temperature of 500°K.

A-57 PV = nRT

P = 3.7 atm

V = 10.2 liter

n = ?

R = 0.082 liter-atm/mole-deg

T = 500°K

$n = \frac{(3.7\ \cancel{\text{atm}})\ (10.2\ \cancel{\text{liter}})\ (\text{mole-}\cancel{\text{deg}})}{(500\ \cancel{°K})\quad (0.082\ \cancel{\text{liter-atm}})} = 0.92\ \text{mole}$

Q-58 A 4.0 g sample of a gas occupies 8.0 liters at STP. What is its volume at 75°C and a pressure of 650 mm of Hg?

A-58 This problem may be solved by two methods

First method

$$\frac{8.0\ \cancel{\text{liter}}}{} \left| \frac{1\ \text{mole}}{22.4\ \cancel{\text{liter}}} \right. = 0.36\ \text{mole}$$

$$\frac{650\ \cancel{\text{mm Hg}}}{} \left| \frac{1\ \text{atm}}{760\ \cancel{\text{mm Hg}}} \right. = 0.85\ \text{atm}$$

$T = 75 + 273 = 348°K$

$$V = \frac{nRT}{P}$$

$$= \frac{(0.36\ \cancel{\text{mole}})(0.082\ \text{liter-}\cancel{\text{atm}})(348\ \cancel{\text{deg}})}{(0.85\ \cancel{\text{atm}})\quad(\cancel{\text{deg-mole}})}$$

$= 12$ liter

Second method

$P_1V_1 = n_1RT_1 \qquad P_2V_2 = n_2RT_2$

$n_1 = n_2 \qquad R = R$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$P_1 = 760$ mm $\qquad P_2 = 650$ mm

$V_1 = 8.0$ liter $\qquad V_2 = ?$

$T_1 = 273°K \qquad T_2 = 348°K$

$$V_2 = \frac{(760\ \cancel{\text{mm}})(8.0\ \text{liter})(348\ \cancel{°K})}{(273\ \cancel{°K})(650\ \cancel{\text{mm}})} = 12\ \text{liter}$$

Q-59 In a particular experiment, 0.0273 mole of O_2 gas was collected over water at 20°C and at a pressure of 715 mm Hg. What volume was occupied by dry oxygen gas?

(vapor pressure of H_2O at 20°C = 17.5 mm Hg)

(Hint: total pressure (715 mm) $= P_{O_2} + P_{H_2O}$)

A-59 $PV = nRT$

$P = (715-17.5)$ mm $= 697$ mm

$$\frac{697\ \cancel{\text{mm Hg}}}{} \left| \frac{1\ \text{atm}}{760\ \cancel{\text{mm Hg}}} \right. = 0.917\ \text{atm}$$

$n = 0.0273$ moles

$R = 0.082$ liter-atom/mole-deg

$T = 273 + 20 = 293°K$

$$V = \frac{(0.0273\ \cancel{\text{mole}})(293\ \cancel{°K})(0.082\ \text{liter-}\cancel{\text{atm}})}{(0.917\ \cancel{\text{atm}})(\cancel{\text{mole-deg}})}$$

$= 0.72$ liter

Q-60 A sample of bromine occupies 2.5 liters at 25°C and 3.4 atm pressure. What will the temperature be when this sample of bromine occupies a volume of 4.0 liters at a pressure of 2.0 atm?

A-60 $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2} \qquad n_1 = n_2$

$P_1 = 3.4$ atm $\qquad P_2 = 2.0$ atm

$V_1 = 2.5$ liter $\qquad V_2 = 4.0$ liter

$T_1 = 25 + 273 = 298°K \qquad T_2 = ?$

$$T_2 = \frac{(2.0\ \cancel{\text{atm}})(4.0\ \cancel{\text{liter}})(298°K)}{(2.5\ \cancel{\text{liter}})(3.4\ \cancel{\text{atm}})}$$

$= 280°K$

Q-61 Using the ideal gas equation, the expression n = mass/MW, where MW = molecular weight, and the expression for density, d = mass/V, derive an equation relating molecular weight to density, pressure, and temperature.

A-61 $PV = nRT$

$n = \text{mass}/MW$

$PV = (RT)(\text{mass})/MW$

$d = \text{mass}/V$

$$P = \frac{(\text{mass})(RT)}{(V)(MW)}$$

$$P = \frac{dRT}{MW} \text{ and } MW = \frac{dRT}{P}$$

Q-62 The density of an unknown gas is 3.6 g/liter at 25°C and 1 atm pressure. What is the molecular weight of the unknown gas?

A-62 $$MW = \frac{dRT}{P}$$

$d = 3.6$ g/liter

$R = 0.082$ liter-atm/mole-deg

$T = 25 + 273 = 298°K$

$P = 1$ atm

$$MW = \frac{(3.6\text{ g})(0.082\ \cancel{\text{liter-atm}})(298\ \cancel{°K})}{(\cancel{\text{liter}})(\cancel{\text{deg}}\text{-mole})(1\ \cancel{\text{atm}})}$$

$= 88$ g/mole

Q-63 In the Dumas method for determining the molecular weight of a gas, the gas density is found by weighing a bulb of known volume filled with the gas. Determine the molecular weight of gas from the data below.

mass of bulb evacuated = 120.270 g

mass of bulb with 1 atm pressure of unknown gas at 25°C = 122.667 g

mass of bulb filled with H_2O at a temperature of 25°C = 631 g

density of H_2O at 25°C = 0.997 g/ml

A-63
$$\begin{array}{rl} 122.667 & \text{(bulb + gas)} \\ -120.270 & \text{(bulb)} \\ \hline 2.397 & \text{g (mass of gas)} \end{array}$$

$$\begin{array}{rl} 631 & \text{(bulb + water)} \\ -120 & \text{(bulb)} \\ \hline 511 & \text{g (mass of } H_2O) \end{array}$$

Volume of flask

$$= \frac{511\ \cancel{\text{g}}\ H_2O}{} \left| \frac{1\ \cancel{\text{ml}}}{0.997\ \cancel{\text{g}}} \right| \frac{1\text{ liter}}{1000\ \cancel{\text{ml}}}$$

$= 0.513$ liter

$$\text{Density of gas} = \frac{2.397\text{ g}}{0.513\text{ liter}}$$

$= 4.67$ g/liter

$$MW = \frac{dRT}{P}$$

$$= \frac{4.67\text{ g}}{\cancel{\text{liter}}} \left| \frac{0.082\ \cancel{\text{liter-atm}}}{\cancel{\text{deg}}\text{-mole}} \right| \frac{298\ \cancel{°K}}{1\ \cancel{\text{atm}}}$$

$= 114$ g/mole

R Gay-Lussac law - ratios of gases involved in a chemical reaction may be expressed as the ratios of small whole numbers provided the gases are at the same temperature and pressure.

Avogadro's principle - equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

Ideal gas equation: $PV = nRT$

PART II: Kinetic Molecular Theory

S-1 A model can be constructed to explain the behavior of gases. This model is given in the form of four concepts known as the Kinetic-molecular Theory which describes ideal gases

a) Gases consist of particles whose total volume is negligible compared to the entire space occupied by a gas
b) There are no attractive forces between particles
c) The particles of a gas are in rapid, random, straight-line motion, colliding with each other and with the walls of their containers. Collisions are perfectly elastic (no loss in energy)
d) The average kinetic energy of the particles of any gas is the same at a given temperature. This energy is dependent only on the absolute temperature

Q-1 In terms of the kinetic molecular theory, explain why the compressibility of gases is so great

A-1 The volume that gas molecules occupy is mostly empty space. Therefore, when a gas is compressed, it is just a reduction of empty space

Q-2 According to the kinetic-molecular theory, what is gas pressure?

A-2 Molecules collide with the walls of the container. Each collision produces a small force and the sum of all the forces per unit area is the pressure

Q-3 In a highly compressed gas, the molecules are close together. When the gas is allowed to expand it occupies all the volume accessible. How does this observation support the second concept of the kinetic-molecular theory?

A-3 In a highly compressed gas any intermolecular forces at work should be greatest since the molecules are closer together. Since the gas expands spontaneously when the volume is increased, there must not be any appreciable binding of one molecule of gas to its neighbors.

Q-4 The average kinetic energy is proportional to the absolute temperature (ke α T).

Kinetic energy can be determined from the expression ke $= \frac{1}{2}mv^2$, where m is the mass of the molecule and v is its velocity. Derive a relationship between absolute temperature and velocity.

A-4 ke α T

ke $= k^*T$ where k^* is a proportionality constant

ke $= \frac{1}{2}mv^2$

Therefore, $\frac{1}{2}mv^2 = k^*T$

$mv^2 = 2k^*T$

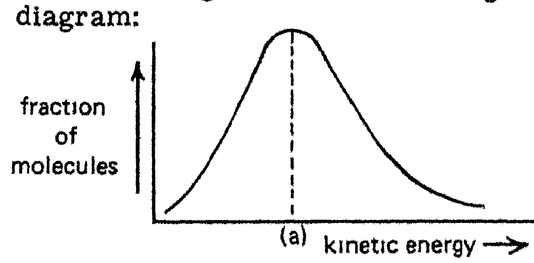
$v^2 = \frac{2k^*T}{m}$

For any given kind of molecule, m is constant. Thus,

$v^2 \ \alpha \ T$

$v \ \alpha \ \sqrt{T}$

Q-5 The kinetic energy of all the molecules in a gas sample is not the same; the average kinetic energy remains the same at a particular temperature. The distribution of kinetic energies follows a well-known statistical distribution curve and is given in the following diagram:



What does each point on the curve indicate?

A-5 Each point tells what fraction of the total number of gas molecules have the kinetic energy value specified

Q-6 In the diagram of Q-5, what would be the most probable value of kinetic energy?

A-6 The most probable value of kinetic energy is the energy corresponding to the maximum on the curve This would be the kinetic energy marked by the letter (a) on the diagram

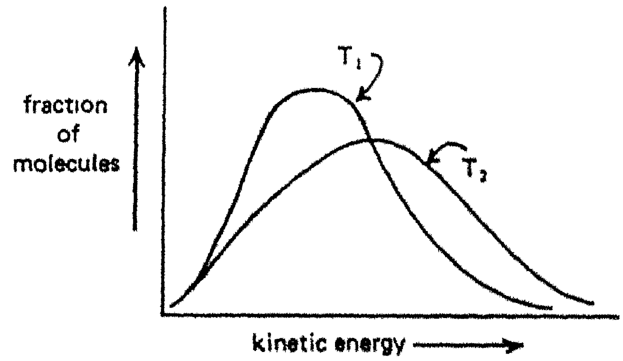
Q-7 If the temperature of a gas increases, what should happen to the total kinetic energy of the gas?

A-7 ke α T. If the temperature increases, the total kinetic energy increases.

Q-8 If the total kinetic energy of the gas increases with increase in temperature, what happens to the value for the most probable value of kinetic energy?

A-8 It increases More molecules would have a higher kinetic energy.

Q-9 Given below are the distribution curves for fraction of molecules vs kinetic energy for a gas sample at two different temperatures. Indicate which curve is for the gas at the higher temperature.

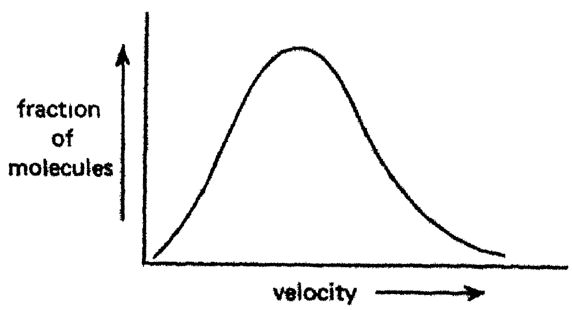


A-9 $T_2 > T_1$

The area under the two curves must be the same because the total number of molecules considered is the same. The molecules are distributed over a greater range of kinetic energies at T_2, with a higher average kinetic energy. At T_2 a smaller fraction of the molecules have the average kinetic energy.

Q-10 With a knowledge of the relationship between kinetic energy and velocity, draw a diagram which shows the distribution of velocities in a gas sample.

A-10



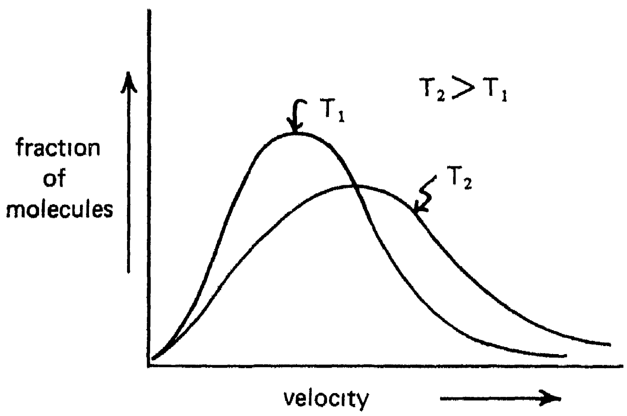
Q-11 What happens to the velocity of molecules as the temperature is raised?

A-11 $v \propto \sqrt{T}$

The velocity increases.

Q-12 Draw the distribution curves for fraction of molecules vs velocity for a gas sample at two different temperatures Indicate which is the higher temperature

A-12



Q-13 Using the kinetic-molecular theory, account for the observed behavior of gases described by Boyle's law ($P=k/V$)

(Hint Pressure is caused by molecular collisions)

A-13 The pressure of a gas depends on the number of particle impacts per unit wall area per second As the size of the containing vessel is reduced, the particles do not have as much volume in which to move Therefore, they collide with the sides of the container more frequently which increases the pressure.

Q-14 Using the kinetic-molecular theory, account for the observed behavior of gases described by Charles' law ($P = kT$)

A-14 Raising the temperature of a gas increases the average velocity of the particles. Therefore, the particles would collide with the sides of the container more frequently, producing a greater pressure.

Q-15 Using the kinetic-molecular theory, account for the observed behavior of gases described by Dalton's law ($P_{total} = P_A + P_B + \; .. \; P_N$)

A-15 There are no attractive forces between the particles of an ideal gas. In a mixture of gases, each particle strikes the walls the same number of times per second as if no other particles were present. Therefore, the pressure of a particular gas in a mixture is not changed by the presence of other gases.

S-2 Gases diffuse into one another because the molecules of the gases are in constant motion. The rate of diffusion depends on the velocity of the molecules. At the same temperature, all gases have the same average kinetic energy given by the equation

$$ke = \frac{1}{2}mv^2,$$

where m is the mass of the molecule and v is the average velocity.

Q-16 Derive an expression for the relative velocity (or rate of diffusion) of molecules with mass m_A compared with those of mass m_B at the same temperature

A-16 At the same temperature, the kinetic energy is the same for the two different molecules,

$$ke_A = ke_B$$

$$\tfrac{1}{2} m_A v_A{}^2 = \tfrac{1}{2} m_B v_B{}^2$$

$$\frac{v_A{}^2}{v_B{}^2} = \frac{\frac{1}{2} m_B}{\frac{1}{2} m_A}$$

$$\frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$$

This is known as Graham's law of diffusion

Q-17 Convert the equation for relative velocity as a function of mass into an equation in which the relative velocity is a function only of molecular weight

(Hint How is the mass of one molecule related to the mass of a mole of molecules?)

A-17 $\frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$

$m_B N = (MW)_B$ where N is Avagadro's number Multiply both the top and bottom of the right side of the equation above by $\sqrt{N}$.

$$\frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}\sqrt{\frac{N}{N}} = \sqrt{\frac{m_B N}{m_A N}}$$

Therefore,

$$\frac{v_A}{v_B} = \sqrt{\frac{(MW)_B}{(MW)_A}}$$

Q-18 What is the relative rate of diffusion for hydrogen molecules compared to those of oxygen at the same temperature.

A-18 $MW_{H_2} = 2$ $\quad MW_{O_2} = 32$

$$\frac{v_{H_2}}{v_{O_2}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

Hydrogen molecules diffuse 4 times faster than oxygen molecules.

Q-19 Two samples of gas are at the same temperature. The molecules of sample A are traveling at twice the speed of the molecules of sample B. What is the relationship between the mass of molecules A and B?

A-19 $\frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$ square both sides

$$\left(\frac{v_A}{v_B}\right)^2 = \frac{m_B}{m_A}$$

$$\left(\frac{2}{1}\right)^2 = \frac{m_B}{m_A} = 4$$

The mass of the molecules in sample B is four times the mass of the molecules in sample A

Q-20 What is the relative velocity of nitrogen molecules compared with those of hydrogen?

A-20 $\frac{v_{N_2}}{v_{H_2}} = \sqrt{\frac{(MW)_{H_2}}{(MW)_{N_2}}}$

$$= \sqrt{\frac{2}{28}}$$

The velocity of nitrogen molecules is $\sqrt{\frac{2}{28}}$ slower than hydrogen molecules

Q-21 A container is filled with a mixture of oxygen and nitrogen each of which have identical partial pressures If a hole is made in the container and gas is allowed to escape, will the escaping gas be richer in nitrogen or oxygen? Why?

A-21 Nitrogen The nitrogen molecules are moving faster than the oxygen molecules and therefore hit the hole more times

Graham's law of diffusion:

$$\frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}} = \sqrt{\frac{(MW)_B}{(MW)_A}}$$

S-3 The average kinetic energy of molecules is related to mass and velocity by the equation, ke = $(\frac{1}{2})mv^2$ The number of collisions which molecules undergo is directly proportional to the average velocity of the molecules and the number of molecules Number of collisions α (average velocity) (number of molecules)

Q-22 A 1 liter sample of H_2 is at 0°C and 1.00 atm (STP) and a 1 liter sample of O_2 is at 0°C and 2.00 atm pressure.

Compare quantitatively the two samples with respect to

a) number of molecules
b) average kinetic energy of the molecules.

A-22 a) PV = nRT

V, R, T are identical

$$\frac{P_{H_2}}{n_{H_2}} = \frac{P_{O_2}}{n_{O_2}}$$

$$\frac{P_{O_2}}{P_{H_2}} = 2 = \frac{n_{O_2}}{n_{H_2}}$$

Since the sample has twice the number of moles of $O_2(n_{O_2})$, it has twice the number of molecules of $O_2(n^*_{O_2})$ as the H_2 sample

b) The temperature of the two gases is the same Therefore, the average kinetic energy of the molecules is the same

Q-23 For the two gas samples in Q-22, compare quantitatively the average speed of the molecules

A-23 a) $ke = \frac{1}{2} mv^2$

Since the gases are at the same temperature

$$\frac{1}{2} m_{H_2} v^2_{H_2} = \frac{1}{2} m_{O_2} v^2_{O_2}$$

$$\frac{v^2_{H_2}}{v^2_{O_2}} = \frac{m_{O_2}}{m_{H_2}} = \frac{MW_{O_2}}{MW_{H_2}}$$

$$\frac{v_{H_2}}{v_{O_2}} = \sqrt{\frac{MW_{O_2}}{MW_{H_2}}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

The average velocity of the H_2 molecules is four times the average velocity of the O_2 molecules.

Q-24 For the two gas samples described in Q-22, compare quantitatively the total number of collisions per second with the walls

A-24 For any gas A,

(number of collisions) α (average velocity)$_A$(number of molecules)$_A$

or $C_A \, \alpha \, v_A n^*_A$

Therefore,

$C_{H_2} \, \alpha \, v_{H_2} n^*_{H_2}$

$C_{O_2} \, \alpha \, v_{O_2} n^*_{O_2}$

and

$$\frac{C_{H_2}}{C_{O_2}} \alpha \left(\frac{v_{H_2}}{v_{O_2}}\right)\left(\frac{n^*_{H_2}}{n^*_{O_2}}\right)$$

$$\frac{C_{H_2}}{C_{O_2}} = \frac{\cancel{k}}{\cancel{k}}\left(\frac{v_{H_2}}{v_{O_2}}\right)\left(\frac{n^*_{H_2}}{n^*_{O_2}}\right)$$

where k is a proportionality constant.

Since $v_{H_2} = 4v_{O_2}$

and $n^*_{H_2} = \frac{n^*_{O_2}}{2}$

$$\frac{C_{H_2}}{C_{O_2}} = \left(\frac{4v_{O_2}}{v_{O_2}}\right)\left(\frac{n^*_{O_2}}{2n^*_{O_2}}\right) = 2$$

number collisions H_2 = (2) number collisions O_2

Q-25 Consider two samples of the same ideal gas in two different 1 liter containers. The pressure of the two samples is equal, but the temperature (in °K) of sample B is half that of sample A. Compare the two samples quantitatively with respect to

a) number of molecules.
b) average kinetic energy of the molecules

A-25 a) $PV = nRT$

P, V, R are identical

$n_A T_A = n_B T_B$

T_A is twice T_B

$$\frac{T_A}{T_B} = 2 = \frac{n_B}{n_A}$$

Sample B has twice the number of particles as sample A

b) Ke α T

T_A is twice T_B

Therefore, the average kinetic energy of sample A is twice that of sample B

Q-26 For the two samples of gas described in Q-25, compare quantitatively the average speed of the particles

A-26 $ke = \frac{1}{2} mv^2$

$m_A = m_B$

$(ke)_A = 2(ke)_B$

$$\frac{v_A{}^2}{v_B{}^2} = \frac{(ke)_A}{(ke)_B} = 2$$

$$\frac{v_A}{v_B} = \sqrt{2}$$

Therefore, the speed of the particles in sample A is $\sqrt{2}$ times faster than those in sample B.

Q-27 For the two gas samples in Q-25, compare quantitatively the total number of collisions per second with the walls.

A-27 $$\frac{\text{Collisions}_A}{\text{Collisions}_B} = \left(\frac{v_A}{v_B}\right)\left(\frac{n^*_A}{n^*_B}\right)$$

$$v_A = \sqrt{2}\, v_b$$

and $n^*_A = \dfrac{n^*_B}{2}$

Thus,

$$\frac{\text{Collisions}_A}{\text{Collisions}_B} = \left(\frac{\sqrt{2}\, v_B}{v_B}\right)\left(\frac{n^*_B}{2n^*_B}\right)$$

$$= \frac{\sqrt{2}}{2}$$

[redacted]

S-4 Real gases deviate from ideal behavior One reason is that the attractive forces between molecules are not negligible The attractive forces existing between molecules are due to

a) dipole-dipole attractions (positive end of one polar bond attracts the negative end of another polar bond)
b) van der Waals forces (motion of electrons in nonpolar molecules give rise to momentary dipoles)
c) hydrogen bonds (hydrogen forms a bridge-bond between two highly electronegative atoms)

Q-28 How would the fact that molecules attract one another cause a gas to deviate from ideal behavior?

A-28 The interaction between molecules of a gas would cause a molecule to collide with the wall of a container with less force Thus, the gas pressure would be less than that expected from an ideal gas.

Q-29 Would the effect produced by molecular attractions be more apparent at high or low temperatures?

A-29 Low temperatures At high temperatures, the high kinetic energy (greater motion) will overcome the forces of attraction

Q-30 If an ideal gas is allowed to expand, no temperature change should be observed because no energy is required to separate the particles. Would a temperature change be expected if a real gas is allowed to expand? Why?

A-30 The gas should cool. Energy is needed to break the force of attraction between the molecules This energy is obtained by absorption of heat.

Q-31 What other factor does the kinetic molecular theory ignore which might cause a gas to deviate from ideality?

A-31 The fact that the actual volume occupied by the particles is not negligible.

Q-32 How would the fact that the actual volume occupied by molecules is not negligible cause a gas to deviate from ideal behavior.

A-32 The volume occupied by a molecule is not available for another molecule. Thus, the free volume (empty space) is less than the volume in which the molecules are contained.

Q-33 Would the fact that the actual volume occupied by molecules is not negligible be more apparent at high or low pressure? Why?

A-33 High pressures. At high pressures the molecules are closer together. The actual volume of the molecules becomes significant compared to the volume in which the molecules are contained. Therefore, the empty space becomes significantly different than the volume of the container.

Q-34 If the radius of an argon atom is 1.54×10^{-8} cm, what per cent of the total volume occupied by one mole of argon gas at STP is empty space? ($V = \frac{4}{3}\pi r^3$)

A-34 Volume of one argon atom =

$$\frac{4}{3}\pi r^3 = \frac{4}{3}(3.14)(1.54\text{x}10^{-8}\text{cm})^3$$

$$= 1.53 \text{ x } 10^{-23}\text{cm}^3/\text{atom}$$

Total volume =

$$(6.02 \text{ x } 10^{23}\ \frac{\text{atoms}}{\text{mole}})(1.53 \text{ x } 10^{-23}\ \frac{\text{cm}^3}{\text{atom}})$$

$$= 9.21 \text{ cm}^3/\text{mole}$$

$$\%\text{ empty space} = \frac{(22,400 \text{ cm}^3 - 9.21 \text{ cm}^3)(100)}{22,400 \text{ cm}^3}$$

= 99.96% or 100% for three significant figures

Q-35 Why do gases approach ideal behavior at low pressures?

A-35 Since the distance between molecules is very large, the forces of attraction between molecules are small. Also, the actual volume of the molecules is negligible compared to the total volume of the container.

Q-36 An equation of state which takes into account the deviation from ideality of a real gas is the van der Waal's equation

$$(V - nb)\left(P + \frac{n^2a}{V^2}\right) = nRT$$

(a and b are constants which are different for each gas.)

Comparing the van der Waal's equation with the ideal gas equation, which term corrects for the volume occupied by the molecules and which term corrects for the forces of attraction between molecules?

A-36 nb volume correction

$\frac{n^2a}{V^2}$ attraction correction

[redacted]

PART III: Liquids

S-1 When the kinetic energy of the molecules in a gas is lowered, the velocity of the molecules decreases. At sufficiently low velocity, the attractive forces between the molecules cause the molecules to coalesce (condense) into a cluster which settles to the bottom of the container as a liquid.

Q-1 What effect would temperature have on the condensation of a gas?

A-1 At a lower temperature, the kinetic energy of the gas molecules is less The attractive forces will eventually overcome the kinetic energy when the temperature becomes low enough Therefore, all gases will condense into a liquid at sufficiently low temperatures

Q-2 What effect would pressure have on the condensation of a gas?

A-2 At high pressures the gas molecules move close together, making the attractive forces between molecules stronger Therefore, increasing pressure tends to condense a gas However, every gas has a <u>critical temperature</u> above which it cannot be condensed into a liquid regardless of how high the pressure is

Q-3 Gas A has strong attractive forces while gas B has weak attractive forces Which gas would be expected to have the <u>highest</u> critical temperature? Why?

A-3 Gas A has the highest critical temperature Because of the strong attractive forces, the temperature required to prevent condensation of gas A would be higher than for gas B

Q-4 Gas C has a critical temperature of 200°K while gas D has a critical temperature of 300°K. Which molecules have the greater attractive forces?

A-4 Molecules of D have the greater attractive forces. Because a higher temperature is required to prevent the condensation of gas D, the attractive forces must be greater between molecules of D than between molecules of C

Q-5 The density of liquid argon is 1.40 g per ml at -186°C. If the argon atom is assumed to be a sphere of radius 1.54×10^{-8}cm, what percentage of liquid argon is apparently empty space? $(V = \frac{4}{3}\pi r^3)$

A-5

$$\frac{1.40\ \cancel{g}}{} \left| \frac{1\ \cancel{mole}}{40\ 0\ \cancel{g}} \right| \frac{6\ 02 \times 10^{23}\ \text{atoms}}{1\ \cancel{mole}}$$

$= 2.11 \times 10^{22}$ atoms

volume of 1 atom $= \frac{4}{3}\pi r^3$

$= \frac{4}{3}\ (3\ 14)(1.54 \times 10^{-8}\ \text{cm})^3$

$= 1.53 \times 10^{-23}\ \text{cm}^3$

volume of 1.40 g of atoms

$= (1.53 \times 10^{-23}\ \text{cm}^3)(2.11 \times 10^{22})$

$= 0\ 323\ \text{cm}^3$

volume of 1.40 g of liquid

$= 1.000\ \text{cm}^3$

% empty space

$= (1.000\ \text{cm}^3 - 0.323\ \text{cm}^3)(100)$

$= 67.7\%$

Q-6 According to the kinetic molecular theory, why should gases be more compressible than liquids?

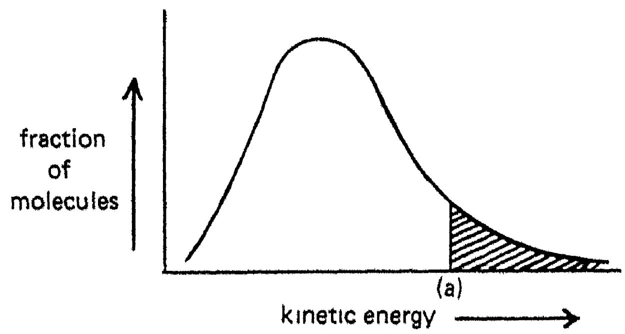
A-6 The amount of free space between the molecules of a liquid is much less than between the molecules of a gas Any attempt to compress the molecules meets with resistance because electron clouds of adjacent molecules repel each other

Q-7 According to the kinetic-molecular theory, why do liquids diffuse very slowly?

A-7 In a liquid, the molecules are very close together and cannot move very far before colliding with neighboring molecules Therefore, diffusion is very slow due to the many collisions that a migrating molecule undergoes

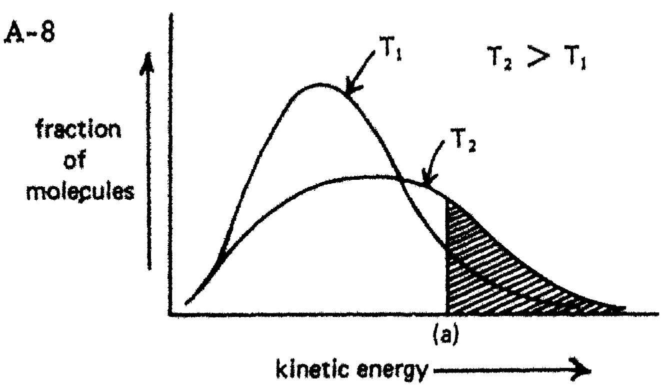
S-2 A molecule of a liquid may at some time have enough kinetic energy to overcome the forces of attraction between neighboring molecules. When this happens, the molecule can escape from its neighboring liquid molecules and become a gas molecule This process is called evaporation

Q-8 The kinetic energy distribution for molecules is the same as for molecules of a gas at the identical temperature The distribution is shown below.



The shaded area represents the fraction of molecules with enough kinetic energy to escape from the liquid. Draw the distribution curve you would expect at a higher temperature and shade in the area that represents the fraction of molecules with enough kinetic energy to escape from the liquid.

A-8



Q-9 Using the distribution plot given in the preceding answer, explain why more molecules escape from the liquid at a higher temperature.

A-9 Since more molecules have enough kinetic energy to overcome the attractive forces between molecules, more will escape

Q-10 When liquid molecules escape into the gaseous state, what can be said about the average energy of the molecules remaining in the liquid state?

(Hint see graph in A-8)

A-10 The kinetic energy of the escaping molecules is greater than the molecules remaining behind Therefore, the average kinetic energy of the molecules in the liquid is less

Q-11 When a molecule escapes from the surface of a liquid, does the temperature of the remaining liquid increase or decrease? Why?

A-11 A decrease in kinetic energy causes a decrease in temperature Since the lower energy molecules remain in the liquid, the temperature must be lower

B **a) Low temperature and high pressure favor condensation of gases.**

b) Critical temperature is the temperature above which a gas cannot be condensed regardless of pressure.

c) Liquids have low compressibility and diffuse slowly.

S-3 If a liquid is placed in a closed container, the liquid evaporates and the pressure above the liquid increases After a period of time the level of the liquid does not change and the pressure does not increase further This apparent lack of change in the system can be explained as follows The gas molecules above the liquid are in constant motion and collide with the surface of the liquid and lose kinetic energy. The decrease in kinetic energy may result in a molecule having insufficient energy to overcome the intermolecular attractions If such a collision occurs the gas molecule becomes a liquid molecule When the rate at which molecules leave the surface of the liquid is equal to the rate at which they return, the system is said to be in <u>equilibrium</u> It is a <u>dynamic equilibrium</u> because, even though no overall change is observed, two exactly equal and opposite changes are occurring.

Q-12 The pressure of the gas molecules above a liquid when equilibrium is obtained at a given temperature is known as the <u>vapor pressure</u> of the liquid substance. How does the vapor pressure of a liquid change with change in temperature? Why?

A-12 The vapor pressure of a liquid increases with increasing temperature because more molecules in the liquid obtain enough kinetic energy to escape. This increases the number of molecules in the gaseous state, thus increasing the pressure.

Q-13 If liquid water is injected into a sealed evacuated container, how does the pressure in the vapor phase depend on the amount of liquid water in the container?

A-13 The vapor pressure is independent of the amount of the liquid phase as long as there is some liquid phase present. The vapor pressure is only dependent on the temperature of the H_2O.

Q-14 Would molecules with high mutual attraction be expected to have a high or low vapor pressure? Why?

A-14 Molecules which have a high mutual attraction have a small tendency to escape into the vapor phase Such a liquid would have a low vapor pressure

Q-15 What kind of attractive forces are possible between molecules in the liquid state?

A-15 Dipole interactions, van der Waal's attractions, hydrogen bonding

Q-16 Consider the following equilibrium vapor pressures at 20°C for the compounds listed below

H_2O	17 5 mm Hg
CCl_4	91 0 mm Hg
$CHCl_3$	160 mm Hg

Which compound has the least and which compound has the greatest intermolecular attraction?

A-16 H_2O greatest

$CHCl_3$ least

Q-17 The boiling point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the external pressure on the surface of that liquid. At which external pressure, 740 or 760 mm of Hg, does H_2O have the higher boiling point? Why?

A-17 760. In order to obtain a vapor pressure of 760 mm Hg, the water must be at a higher temperature than that necessary to obtain a vapor pressure of 740 mm Hg

Q-18 In order to avoid ambiguity, it is necessary to define a standard, or normal boiling point The normal boiling point is the temperature at which the vapor pressure of a liquid is equal to one atmosphere

What would be predicted for the relationship between normal boiling point and attractive forces between the molecules of a liquid?

A-18 The higher the normal boiling point, the greater the attractive forces between the molecules of a liquid.

Q-19 Given the following normal boiling points

CS_2	46.3°C
H_2O	100 0°C
CCl_4	77.0°C

In which liquid are the intermolecular attractive forces weakest?

A-19 CS_2

Q-20 Is the equilibrium vapor pressure of water measured at 25°C at sea level greater than, less than or the same as that measured at 25°C at an elevation of 1 mile?

A-20 Same as The vapor pressure of a liquid is a function of the temperature of the liquid

Q-21 Is the boiling point of water measured at sea level greater than, less than, or the same as that measured at an elevation of 1 mile?

A-21 Greater than.

Q-22 Is the normal boiling point of water measured at sea level greater than, less than, or the same as that measured at an elevation of 1 mile?

A-22 Same as The normal boiling point is the temperature at which the vapor pressure of a liquid is equal to one atmosphere pressure

Q-23 The normal boiling point of liquid HCl is -84°C At this temperature, the vapor pressure of SO_2 is less than 10 mm Hg. Are the intermolecular attractions greater in liquid SO_2 or liquid HCl?

A-23 Greater in liquid SO_2.

Q-24 In a series of similar compounds (for instance C_2H_6, C_3H_8, C_4H_{10}) the normal boiling point is highest for the compound of greatest molecular weight. Why?

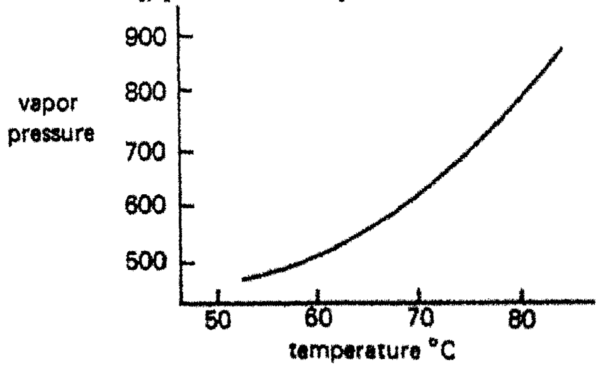
A-24 The higher the molecular weight, the more atoms there are present in the molecule and thus the number of attractive forces among the molecules are greater

Q-25 Which compound would be expected to have the highest normal boiling point?

C_2H_6, C_3H_8, CH_4

A-25 C_3H_8

Q-26 From the graph below, find the normal boiling point for ethyl alcohol.



A-26 Normal boiling point at 760 mm Hg = 78°C.

B a) Dynamic equilibrium - no overall change is observed but equal and opposite changes are occurring

b) Vapor pressure depends on

[illegible]

PART IV: Solids

S-1 When the temperature of liquid molecules is reduced, a temperature is eventually reached at which the attractive forces between the molecules are strong enough to hold them in fixed positions and a solid forms In solids the molecules are arranged in definite geometric patterns In the solid state the molecules are not stationary, but their motion is very restricted

Q-1 When a solid changes into a liquid, the process is called melting The temperature at which the melting occurs is called the melting point In terms of the kinetic-molecular theory account for the fact that solids melt when the temperature reaches a high enough value

A-1 The molecules in a solid vibrate about a fixed position When the temperature is increased, their kinetic energy is increased, causing the molecules to vibrate more rapidly. A temperature is reached (melting point) where the intermolecular attractive forces can no longer hold the vibrating molecules, thus allowing them to slip out of their rigid position in the solid lattice

Q-2 The density of solid argon is 1 65 g per ml at -233 °C If the argon atom is assumed to be a sphere of radius 1 54 x 10^{-8} cm($V = \frac{4}{3}\pi r^3$), what percentage of solid argon is apparently empty space? Compare with gaseous argon A-34, Part III

A-2 $\frac{1.65\ \cancel{g}}{} \left| \frac{1\ \cancel{mole}}{40\ 0\ \cancel{g}} \right| \frac{6\ 02 \times 10^{23}\ atoms}{1\ \cancel{mole}}$

$= 2.48 \times 10^{22}$ atoms

Volume of one atom from A-34, part III

$= 1.53 \times 10^{-23}\ cm^3$

Volume of 1.65 g of atoms

$= (1.53 \times 10^{-23})(2.48 \times 10^{22}\ atoms)$

$= 0.379\ cm^3$

Volume of 1 65 g of solid = 1.000 cm^3

% empty space

$= (1.000\ cm^3 - 0.379\ cm^3)(100)$

= 62 1%

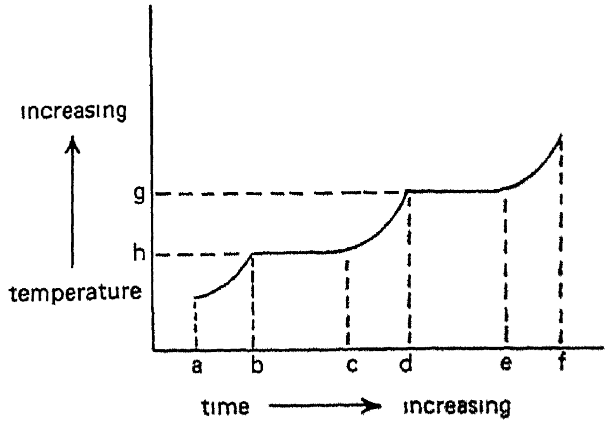
Q-3 In terms of the kinetic-molecular theory, account for the fact that solids are essentially incompressible, whereas gases are easily compressed.

A-3 In solids the molecules are in contact with each other, leaving very little free volume. However, gas molecules are far apart, leaving considerable free volume into which the molecules can be compressed.

Q-4 In terms of the kinetic-molecular theory account for the fact that diffusion in solids is many times slower than in liquids.

A-4 In the solid state molecules have permanent positions from which they do not move far, whereas molecules in the liquid state are free to slide over each other to take up different positions

Q-5 Consider the following heating curve for a substance



If heat is added at a constant rate, the increase in temperature of the solid with time is indicated by the line ab. The line bc represents the time when heat is added to the solid and liquid which are at equilibrium at the melting temperature, h The temperature does not increase along the line bc because the heat added is used to do work against attractive forces in the crystal when the crystal melts. Is the kinetic energy of the solid and liquid the same at b and c?

A-5 Yes According to the kinetic-molecular theory, if the temperature is the same, the kinetic energy must be the same

Q-6 Energy is required to convert a solid at its melting point into a liquid. Why? (Hint: Are the attractive forces stronger in the solid or the liquid state?)

A-6 Since the attractive forces are stronger in the solid, energy is required to disrupt these forces in order to convert the solid to the liquid.

Q-7 Is the potential energy the same at b and c?

A-7 No The potential energy increases because work is done against attractive forces in the crystal.

Q-8 What does the line cd represent?

A-8 The line cd represents the increase in temperature of the liquid with time.

Q-9 What does the temperature g represent?

A-9 The temperature g is the boiling temperature of the liquid.

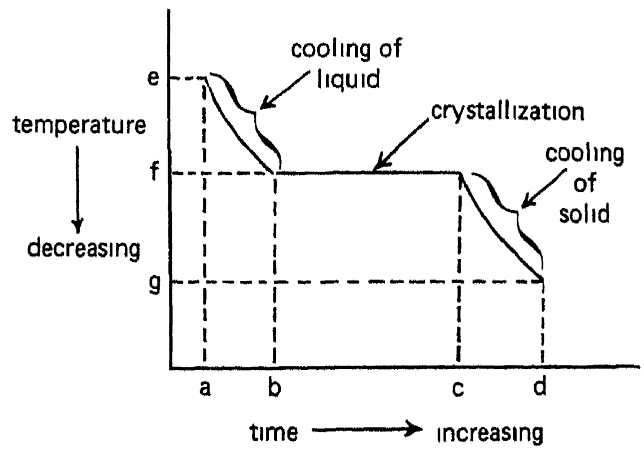
Q-10 Why doesn't the temperature increase along the line de?

A-10 The temperature doesn't increase because at the boiling point the heat added does not increase the kinetic energy, but does increase the potential energy. The potential energy is increased because work is done against attractive forces in the liquid when the liquid boils.

Q-11 What does the line ef represent?

A-11 The line ef represents the increase in temperature of the gas with time

Q-12 When a liquid crystallizes, the temperature remains constant until all the liquid has solidified. A cooling curve (temperature vs time) for the crystallization of a liquid is given below



At what time does solid first begin to form?

A-12 At time b

Q-13 In the graph of temperature vs time for the cooling curve, at what time does all the liquid become solid?

A-13 At time c

Q-14 In the graph of Q-12, at what temperature do the solid and liquid states exist in equilibrium? What is the temperature called?

A-14 At temperature f, solid and liquid states exist in equilibrium. This temperature is called the freezing point of the liquid or the melting point of the solid.

Q-15 When a liquid at temperature f changes into a solid at the same temperature, energy is given off. When a solid at temperature f changes to a liquid at the same temperature energy is absorbed. If the energy released in crystallization is called the heat of crystallization, what is the energy absorbed called.

A-15 The heat of melting or, more commonly, the heat of fusion.

Q-16 Will the energy released in crystallization be equal to, greater than or less than the energy absorbed in melting?

A-16 Equal to.

Q-17 As energy is removed from a liquid its temperature decreases until the freezing point is reached. Continued removal of energy does not cause a decrease in temperature of the solid-liquid mixture until all of the liquid is frozen. Why?

A-17 When the particles crystallize the potential energy decreases and the energy is released as heat which compensates for the energy removed

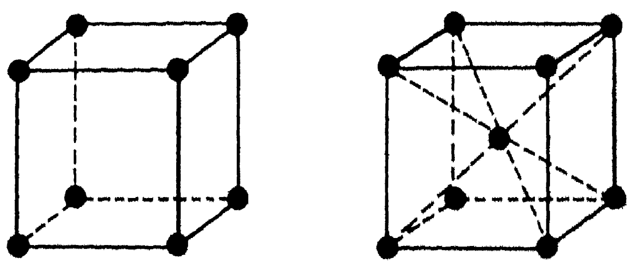
R a) The molecules in a solid are [illegible] fixed positions.

b) Solids are essentially [illegible] and diffuse very slowly.

c) The melting point of a solid is [illegible] temperature at which solid and liquid exist in equilibrium [illegible] pressure of solid and liquid [illegible] equal).

d) [illegible]

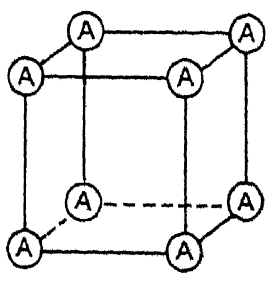
S-2 Unlike gases or liquids, substances in the solid state are characterized by a definite geometrical arrangement of particles within the solid. The three dimensional arrangement of particles gives rise to a crystal lattice which can be determined by X-ray study. The pattern which is repeated to give the crystal lattice is called the unit cell. The simplest type of unit cell system has a cubic pattern There are three types of cubic cells: simple cubic, body-centered cubic and face-centered cubic. In the drawing below, the radii of the atoms are greatly reduced for clarity



simple cubic body-centered cubic face-centered cubic

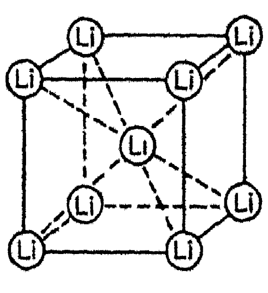
Q-18 Draw the unit cell for a metal, A, which has a simple cubic crystal structure

A-18



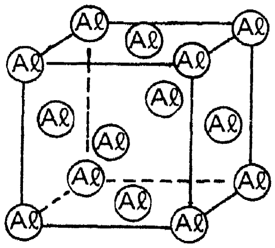
Q-19 Li metal has a body-centered cubic structure. Draw the unit cell for Li metal.

A-19



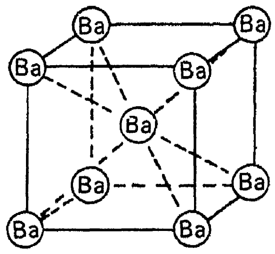
Q-20 Al metal has a face-centered cubic structure. Draw the unit cell for Al metal.

A-20



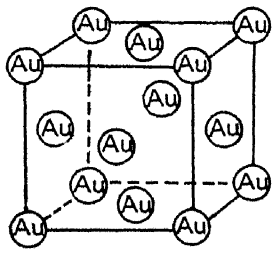
Q-21 Ba metal has a body-centered cubic structure Draw the unit cell of Ba metal

A-21



Q-22 Gold (Au) has a face-centered cubic structure Draw the unit cell of gold

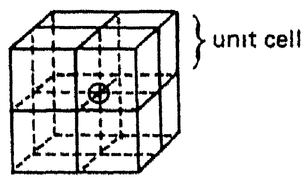
A-22



1) Unit cell - smallest repeat[illegible] of a crystal

2) Cubic structures
a) simple
b) body-centered
c) face-centered

S-3 In a simple cubic unit cell each atom occupying a lattice site of the cell is shared by eight unit cells



Therefore, each atom contributes 1/8 of itself to any one unit cell

Q-23 If an element has a simple cubic unit cell, how many atoms of the element are in each unit cell?

A-23 Eight atoms (one at each corner of the cube) contribute 1/8 of an atom to the cell.

Therefore, each unit cell contains

1/8 (8 atoms) = 1 atom

Q-24 In a body-centered cubic unit cell each atom occupying the corners of the cell is shared by eight unit cells. The atom in the center of a cell is part of only one unit cell.

If cesium metal has a body-centered cubic structure, how many atoms are in each unit cell?

A-24 1/8 (8 atoms at corners) = 1 atom

1 atom at the center = 1 atom

2 atoms in each unit cell

Q-25 In a face-centered cubic unit cell, each atom occupying the corners of the cell is shared by eight cells. The atoms at the face of the cube are shared by two unit cells.

How many faces are there in a cube?

A-25 Six

Q-26 What is the total contribution to each cell of all the atoms on the faces of a face-centered cubic unit cell?

A-26 1/2 (6 atoms at faces) = 3 atoms

Q-27 If copper metal has a face-centered cubic structure, how many atoms of Cu are in each unit cell?

A-27 1/8 (8 atoms at corners) = 1 atom

1/2 (6 atoms at faces) = 3 atoms

4 atoms in each unit cell

Q-28 The dimensions of cubic unit cells are usually given in Angstrom units (10^{-8} Å = 1 cm) What is the volume of a cubic unit cell with one edge equal to 2 Å?

A-28 Volume = $(2\ \text{Å})^3 = 8\ \text{Å}^3$

Q-29 Vanadium metal has a body-centered cubic structure and the length of the unit cell is 3.04 Å. Calculate the volume of the unit cell in cubic centimeters.

A-29 Volume = $(3.04\ \text{Å})^3 = 28.1\ \text{Å}^3$/unit cell

$1\ \text{Å} = 10^{-8}$ cm

Thus,

$$\text{volume} = \frac{28.1\ \cancel{\text{Å}^3}}{1\ \text{unit cell}} \cdot \frac{10^{-24}\ \text{cm}^3}{1\ \cancel{\text{Å}^3}} = 2.81 \times 10^{-23}\ \text{cm}^3$$

Q-30 Vanadium has a density of 5.96 g/cm³. Calculate the mass of one unit cell.

A-30
$$\frac{5.96\ \text{g}}{\cancel{\text{cm}^3}} \cdot \frac{2.81 \times 10^{-23}\ \cancel{\text{cm}^3}}{\text{unit cell}} = 1.67 \times 10^{-22}\ \text{g/unit cell}$$

Q-31 How many vanadium atoms are in each unit cell of the element? (Vanadium has a body-centered cubic structure.)

A-31 1/8 (8 atoms at corners) = 1 atom

1 atom at center = 1 atom

2 atoms

Q-32 **Calculate the mass of one vanadium atom using the data from A-30 and A-31.**

A-32
$$\frac{1.67 \times 10^{-22}\ \text{g}}{1\ \cancel{\text{unit cell}}} \cdot \frac{1\ \cancel{\text{unit cell}}}{2\ \text{atom}} = 8.35 \times 10^{-23}\ \text{g/atom}$$

Q-33 **From the data obtained in A-32, calculate the mass of one mole of vanadium atoms (atomic weight).**

A-33
$$\frac{8.35 \times 10^{-23}\ \text{g}}{1\ \cancel{\text{atom}}} \cdot \frac{6.02 \times 10^{23}\ \cancel{\text{atom}}}{1\ \text{mole}} = 50.3\ \text{g/mole}$$

(actual atomic weight = 50.9)

Q-34 **Molybdenum (Mo) has a body-centered structure and a density of 10.2 g/cm³. The length of each unit cell is 3.14 Å. Calculate the atomic weight of Mo from this data.**

A-34
$$\frac{(3.14\ \cancel{\mathring{\mathrm{A}}})^3}{\cancel{\text{unit cell}}}\left|\frac{10^{-24}\ \cancel{\text{cm}^3}}{1\ \cancel{\mathring{\mathrm{A}}^3}}\right|\frac{10.2\ \text{g}}{\cancel{\text{cm}^3}}\left|\frac{\cancel{\text{unit cell}}}{2\ \cancel{\text{atom}}}\right|\frac{6.02 \times 10^{23}\ \cancel{\text{atom}}}{1\ \text{mole}}$$

= 95.0 g/mole

(actual atomic weight = 95.9)

Q-35 Lithium (Li) metal has a body-centered cubic structure, a unit cell 3.50 Å on a side, a density of 0.53 g/cm^3 and an atomic weight of 6.94 g/mole. From this data, calculate a value for Avogadro's number.

(Hint: First calculate the volume (in Å^3) of a mole of Li atoms, and then the number of unit cells in a mole of Li atoms.)

A-35
$$\frac{6.94\ \cancel{\text{g Li}}}{1\ \text{mole Li}}\left|\frac{1\ \cancel{\text{cm}^3}}{0.53\ \cancel{\text{g}}}\right|\frac{1\ \cancel{\mathring{\mathrm{A}}^3}}{10^{-24}\ \cancel{\text{cm}^3}}\left|\frac{1\ \cancel{\text{unit cell}}}{(3.50\ \cancel{\mathring{\mathrm{A}}})^3}\right|\frac{2\ \text{atoms}}{1\ \cancel{\text{unit cell}}}$$

= 6.2 x 10^{23} atoms/mole

Avogadro's number (actual value) = 6.02 x 10^{23}

Q-36 Aluminum metal has a face-centered cubic structure. How many Al atoms are in each unit cell of the element?

A-36 1/8 (8 atoms at corners) = 1 atom
1/2 (6 atoms at faces) = 3 atoms
4 atoms in each unit cell.

Q-37 Al has a unit cell 4.04 Å on a side and a density of 2.70 g/cm^3. Calculate the atomic weight of Al metal.

A-37
$$\frac{(4.04\ \cancel{\mathring{\mathrm{A}}})^3}{1\ \cancel{\text{unit cell}}}\left|\frac{10^{-24}\ \cancel{\text{cm}^3}}{1\ \cancel{\mathring{\mathrm{A}}^3}}\right|\frac{2.70\ \text{g}}{\cancel{\text{cm}^3}}\left|\frac{1\ \cancel{\text{unit cell}}}{4\ \cancel{\text{atoms}}}\right|\frac{6.02 \times 10^{23}\ \cancel{\text{atoms}}}{1\ \text{mole}}$$

= 26.8 g/mole

(actual atomic weight = 26.98)

Q-38 Ag metal has a face-centered structure, a density of 10.5 g/cm^3 and an atomic weight of 108 g/mole. Calculate the mass of a unit cell of Ag metal.

A-38
$$\frac{108\ \text{g Ag}}{1\ \cancel{\text{mole}}}\left|\frac{1\ \cancel{\text{mole}}}{6.02 \times 10^{23}\ \cancel{\text{atoms}}}\right|\frac{4\ \cancel{\text{atoms}}}{1\ \text{unit cell}}$$

= 71.8 x 10^{-23} g Ag/unit cell

Q-39 From the data in Q-38 and A-38, calculate the length of an edge of a unit cell of Ag metal.

A-39
$$\frac{71.8 \times 10^{-23}\ \cancel{\text{g Ag}}}{\text{unit cell}}\left|\frac{1\ \cancel{\text{cm}^3}}{10.5\ \cancel{\text{g Ag}}}\right|\frac{1\ \mathring{\mathrm{A}}^3}{10^{-24}\ \cancel{\text{cm}^3}}$$

= volume of the unit cell

= 68.4 Å^3

length of an edge of the cell = $\sqrt[3]{68.4\ \mathring{\mathrm{A}}^3}$

= 4.09 Å

The length of the unit cell determined by X-ray is 4.077 Å.

Q-40 Gold has a face-centered cubic structure, a unit cell 4.07 Å on a side, a density of 19.3 g/cm^3, and an atomic weight of 197 g/mole. Calculate a value for Avogadro's number from this data.

A-40 $\dfrac{197\ \cancel{g\ Au}}{1\ \text{mole Au}} \times \dfrac{\cancel{cm^3}}{19.3\ \cancel{g}} \times \dfrac{1\ \cancel{Å^3}}{10^{-24}\ \cancel{cm^3}} \times \dfrac{1\ \cancel{\text{unit cell}}}{(4.07\ \cancel{Å})^3} \times \dfrac{4\ \text{atoms}}{1\ \cancel{\text{unit cell}}}$

$= 6.06 \times 10^{23}$ atoms/mole

Avogadro's number (actual value) = 6.02×10^{23}

R **Any <u>one</u> of the following constants for a crystal may be calculated provided the type of crystal lattice and all the other constants are known.**

a) dimensions of the unit cell
b) density
c) atomic weight
d) Avogadro's number

S-4 Based upon the nature of the particles which occupy the lattice points and the forces holding a lattice together, crystal structures may be classed as: metallic, ionic, molecular or covalent. All crystals discussed so far have been metallic.

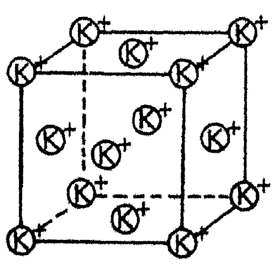
TYPE OF CRYSTAL	PARTICLES AT THE LATTICE SITES	FORCE HOLDING LATTICE TOGETHER
covalent	atoms	covalent
ionic	positive and negative ions	electrostatic
metallic	metal ions	attraction between metal ions and electrons surrounding the metal ions
molecular	molecules	van der Waals, dipole-dipole, hydrogen bonds

Q-41 What type of crystal is KCl? What particles occupy the lattice points?

A-41 Ionic crystal. K^+ ions and Cl^- ions occupy the lattice sites and the ions are held by electrostatic forces.

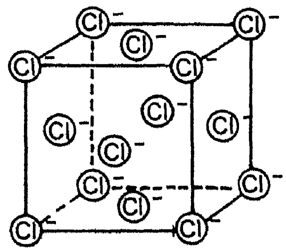
Q-42 KCl has a cubic structure. Sketch a face-centered cube showing only K^+ ions at the lattice sites.

A-42



Q-43 Sketch a face-centered cube showing only Cl^- ions at the lattice sites.

A-43



Q-44 The structure of KCl consists of interpenetrating cubes with lattice sites as drawn in A-42 and A-43

The two alternative unit cells of KCl are illustrated below Note that figure I has K^+ ions at the points of a face-centered cube with Cl^- ions equidistant between K^+ ions, and that Figure II shows Cl^- ions at the points of face-centered cube with K^+ ions equidistant between Cl^- ions

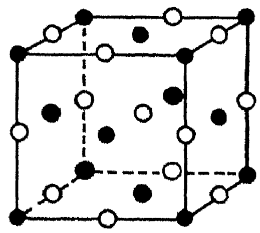


Figure I

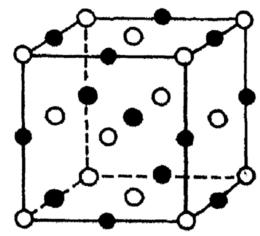


Figure II

● = K^+

○ = Cl^-

According to Figure I, how many K^+ ions are in the unit cell?

A-44 1/8 (8 K^+ ions at corners) = 1 K^+ ion

1/2 (6 K^+ ions at faces) = 3 K^+ ions

4 K^+ ions

Q-45 Ions at the edge of a cube contribute $\frac{1}{4}$ of an ion to a unit cell. How many Cl^- ions are in the unit cell in Figure I. (Don't forget the Cl^- ion in the center of the cube.)

What is the ratio of K^+ ions to Cl^- ions in the unit cell of KCl?

A-45 1/4 (12 Cl^- ions on edges) = 3 Cl^- ions

One Cl^- ion at center = 1 Cl^- ion

4 Cl^- ions

$$\frac{\text{number of } K^+ \text{ ions}}{\text{number of } Cl^- \text{ ions}} = \frac{4}{4} = 1$$

Q-46 According to Figure II, what is the ratio of K^+ ions to Cl^- ions?

A-46 1/4 (12 K^+ ions on edges) = 3 K^+ ions

One K^+ ion at center = 1 K^+ ion

4 K^+ ions

1/8 (8 Cl^- ions at corners) = 1 Cl^- ion

1/2 (6 Cl^- ions at faces) = 3 Cl^- ions

4 Cl^- ions

. ratio of K^+ to Cl^- = 1:1

Q-47 What type of crystal is ice?

(H_2O molecules occupy the lattice sites.)

A-47 **Molecular**

Q-48 What type of crystal is H_2?

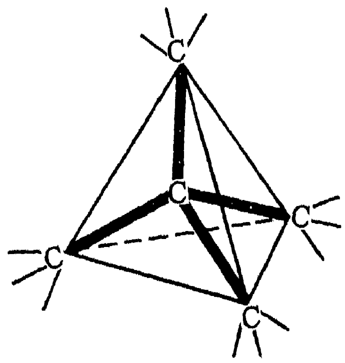
A-48 **Molecular**

Q-49 What type of crystal is diamond (carbon atoms are joined by covalent bonds)?

A-49 Covalent

Q-50 In the diamond structure each carbon atom is bonded to four other carbon atoms in a tetrahedral arrangement. Sketch the diamond crystal structure

A-50



This is only part of the unit cell of carbon

R Covalent crystals - atoms bound by covalent bonds

Ionic crystals - positive and negative ions bound by electrostatic forces

Metallic crystals - metal ions bound by attractions between metal ions and electrons

Molecular crystals - molecules bound by van der Waals, dipole-dipole forces, and hydrogen bonds

S-5 Because of the different types of forces holding crystals together (see S-4), in general, the lattice strength decreases according to the type of crystal structure in the following order:

covalent > ionic > metallic > molecular

Q-51 Strong binding forces in a crystal make the crystal hard and high melting.

According to the information given in S-5, which type of crystal should be the hardest and have the highest melting point?

A-51 Covalent crystals. (The hardest substance known is diamond - a covalent crystal.)

Q-52 Which type of crystal should be the softest and have the lowest melting point?

A-52 Molecular (Many molecular crystals have such low melting points that the substance is a gas at room temperature, e.g. - H_2.)

Q-53 Electrical conductivity of a solid requires that the solid have mobile electrons.

Which type of crystal should be a good electrical conductor?

A-53 The "sea of electrons" surrounding the metal ions at the lattice points is very mobile; therefore, the electrical conductivity of metallic solids is very high

Q-54 Metals are also good conductors of heat. How does the metallic theory of bonding account for this?

A-54 The thermal energy could be transported from one part of the solid to the other by the mobile electrons

Q-55 Would the attractive forces in a metal be directional (oriented in one specific direction) or non-directional (uniform in all directions)? (Hint The lattice site, occupied by a metal ion, is surrounded by a "sea of electrons ")

A-55 Non-directional, because the metallic ion is surrounded by electrons all of which are equivalent

Q-56 If the attractive forces in a metallic crystal are non-directional, will there be any strongly preferred position for the metallic ion?

A-56 No. The metallic ion will feel the same attractive forces in many different positions It should be easy to move a metallic ion from one position to another

Q-57 Metals are malleable (easily flattened into sheets) and ductile (easily drawn into wire) How can these properties be accounted for in terms of the metallic theory of bonding?

A-57 If the forces holding the metal together are non-directional, the metal ions can be moved fairly easily from one lattice site to another Thus, flattening the metal or drawing it into wire does not require the breaking of any strong attractive forces.

R Lattice strength in different types of crystals decreases in the following order:

covalent > ionic > [illegible]

NOTES

Chapter 6 | *COLLIGATIVE PROPERTIES*

Part I <u>Solutions of Miscible Liquids</u>

After completing this section you should

a) be able to calculate the mole fraction of the components of a solution
b) understand the relationship of the mole fraction of a component of a solution to its partial vapor pressure (Raoult's law)
c) understand the relationship of partial vapor pressure to total vapor pressure
d) understand the relationship of the mole fraction of a component in the vapor phase to its mole fraction in the liquid phase
e) understand boiling point diagrams and fractional distillation.

Part II: <u>Solutions of Nonvolatile Solutes</u>

After completing this section you should

a) understand the effect of a nonvolatile solute on the vapor pressure, boiling point, and freezing point of a liquid
b) be able to calculate the molecular weight and percent dissociation of a solute from colligative property data
c) understand the nature of osmotic pressure.

PART I: Solutions of Miscible Liquids

S-1 In a solution of two mutually soluble liquids the concentration of each component can be expressed as the <u>mole fraction</u>. The mole fraction is the number of moles of the component present divided by the total number of moles of all the components present in a solution (including the solvent).

Q-1 Write an expression for the mole fraction X_A, of component A, for a solution containing n_A moles of A and n_B moles of B.

A-1
$$X_A = \frac{n_A}{n_A + n_B}$$

Q-2 What must be the sum of the mole fractions of the components of a solution?

A-2 $X_A + X_B = 1$ or

$X_A + X_B + \ldots + X_Z = 1$

Q-3 A solution contains 1.00 mole of ethyl bromide, CH_3CH_2Br, and 3.00 moles of propyl bromide, $CH_3CH_2CH_2Br$. What is the mole fraction of ethyl bromide?

A-3
$$X_{\text{ethyl bromide}} = \frac{n_{\text{ethyl bromide}}}{n_{\text{propyl bromide}} + n_{\text{ethyl bromide}}}$$
$$= \frac{1.00 \text{ mole}}{3.00 \text{ mole} + 1.00 \text{ mole}} = \frac{1.00}{4.00}$$
$$= 0.250$$

Q-4 A solution contains 2.80 moles of acetone, CH_3COCH_3, and 8.20 moles of chloroform, $CHCl_3$. Calculate the mole fraction of acetone.

A-4
$$X_{\text{acetone}} = \frac{n_{\text{acetone}}}{n_{\text{acetone}} + n_{\text{chloroform}}}$$
$$= \frac{2.80 \text{ mole}}{2.80 \text{ mole} + 8.20 \text{ mole}}$$
$$= 0.254$$

Q-5 What is the mole fraction of chloroform in the solution of Q-4?

A-5 $X_{\text{acetone}} + X_{\text{chloroform}} = 1.000$

$$X_{\text{chloroform}} = 1.000 - X_{\text{acetone}}$$
$$= 1.000 - 0.254$$
$$= 0.746$$

Q-6 Calculate the mole fraction of all the components of a solution which contains the following liquids.

CH_3COCH_3, acetone	0.250 mole
$CHCl_3$, chloroform	0.750 mole
C_6H_6, benzene	0.900 mole

A-6

$$X_{acetone} = \frac{n_{acetone}}{n_{acetone} + n_{chloroform} + n_{benzene}}$$

$$= \frac{0.250 \text{ mole}}{0.250 \text{ mole} + 0.750 \text{ mole} + 0.900 \text{ mole}}$$

$$= \frac{0.250}{1.90} = 0.132$$

$$X_{chloroform} = \frac{0.750}{1.90} = 0.395$$

$$X_{acetone} + X_{chloroform} + X_{benzene} = 1.000$$

$$X_{benzene} = 1.000 - X_{chloroform} - X_{acetone}$$

$$= 1.000 - 0.131 - 0.394$$

$$= 1.000 - 0.525$$

$$= 0.475$$

Q-7 A solution is made by mixing 7.80 grams of benzene, C_6H_6, and 46.0 grams of toluene, $CH_3C_6H_5$.

Calculate the mole fraction of benzene in the solution.

$MW_{benzene} = 78.0$

$MW_{toluene} = 92.1$

A-7 First, calculate the moles of benzene and toluene present.

$$\frac{7.80 \cancel{\text{ g benzene}}}{} \left| \frac{1 \text{ mole benzene}}{78.0 \cancel{\text{ g benzene}}} \right.$$

$= 0.100$ mole benzene

$$\frac{46.0 \cancel{\text{ g toluene}}}{} \left| \frac{1 \text{ mole toluene}}{92.1 \cancel{\text{ g toluene}}} \right.$$

$= 0.500$ mole toluene

$$X_{benzene} = \frac{n_{benzene}}{n_{benzene} + n_{toluene}}$$

$$= \frac{0.100 \text{ mole}}{0.100 \text{ mole} + 0.500 \text{ mole}}$$

$$= \frac{0.100}{0.600} = 0.167$$

[redacted]

S-2 **Just as it is possible to describe an ideal gas, it is also possible to describe an <u>ideal solution</u> and predict its properties from theoretical considerations. In an ideal solution the various pure components do not experience any change in properties other than dilution. In an ideal solution of two or more volatile liquids at a given temperature, each liquid establishes a partial vapor pressure which is equal to the vapor pressure of the pure liquid multiplied by the mole fraction of that liquid in the solution. This is a statement of <u>Raoult's Law</u>.**

Q-8 If P_A° is the vapor pressure of pure A, write an expression for the partial pressure of A, P_A, in terms of P_A° and X_A.

A-8 $P_A = P_A^\circ X_A$

Q-9 If P_B° is the vapor pressure of pure B, write an expression for partial pressure of B, P_B, in terms of P_B° and X_B in an ideal solution.

A-9 $P_B = P_B^\circ X_B$

Q-10 If the vapor pressure of pure A is 234 mm Hg at 20°C, what is the partial vapor pressure of A above an ideal solution at 20°C if the mole fraction of A is equal to 0.250?

A-10 $P_A = P_A^\circ X_A$

$= (234 \text{ mm Hg})(0\ 250)$

$= 58.5 \text{ mm Hg}$

Q-11 The vapor pressure of pure ethylene dibromide, $C_2H_4Br_2$, at 85°C is 170 mm Hg. Calculate the partial vapor pressure of ethylene dibromide above an ideal solution at 85°C with a mole fraction of ethylene dibromide of 0.250.

A-11 $P_{C_2H_4Br_2} = P^\circ_{C_2H_4Br_2}\ X_{C_2H_4Br_2}$

$= (170 \text{ mmHg})(0.250)$

$= 42\ 5 \text{ mm Hg}$

Q-12 Calculate the partial pressure of $C_2H_4Br_2$ at 85°C for an ideal solution with a mole fraction of $C_2H_4Br_2$ of 0.500 and 0.750.

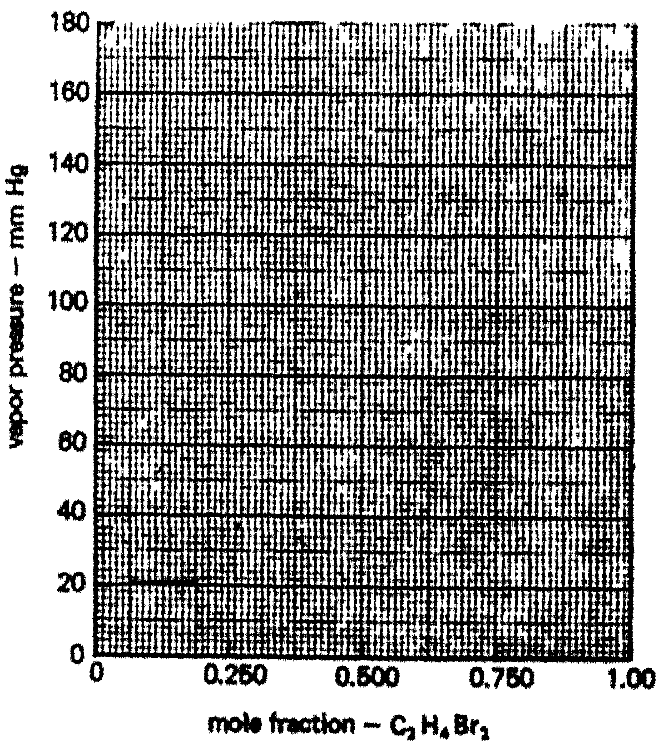
A-12 $P_{C_2H_4Br_2} = (170 \text{ mm Hg})(0.500)$

$= 85.0 \text{ mm Hg}$

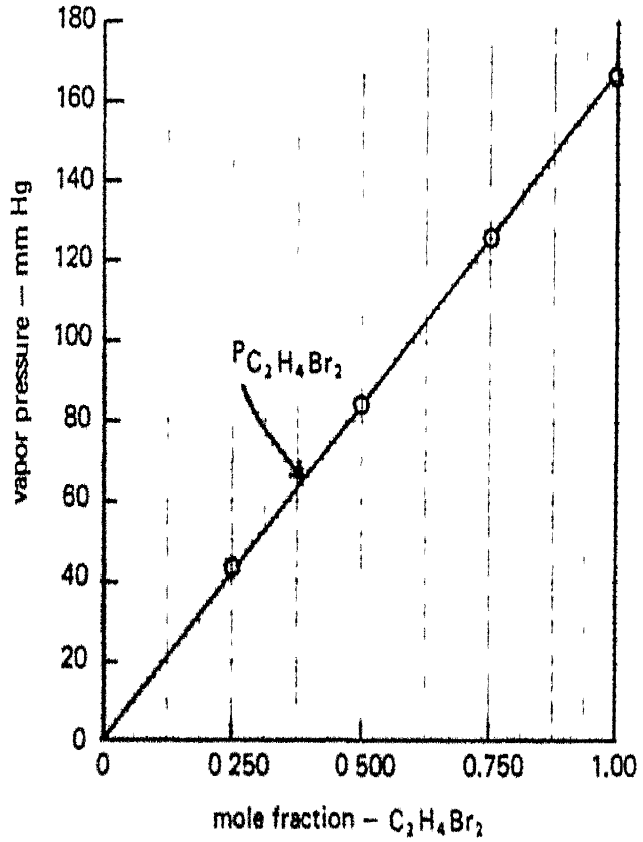
$P_{C_2H_4Br_2} = (170 \text{ mm Hg})(0.750)$

$= 128 \text{ mm Hg}$

Q-13 Plot the values for the vapor pressure of $C_2H_4Br_2$ calculated in A-11 and A-12 on the figure below. It should be emphasized that the graph to be plotted will be total vapor pressure versus mole fraction for a two component solution in which temperature remains constant.



A-13



Q-14 The vapor pressure of pure propylene dibromide, $C_3H_6Br_2$, at 85°C is 130 mm Hg.

Assuming ideal behavior, calculate the partial vapor pressure of $C_3H_6Br_2$ for the following solutions at 85°C·

a) $X_{C_3H_6Br_2} = 0.250$

b) $X_{C_3H_6Br_2} = 0\ 500$

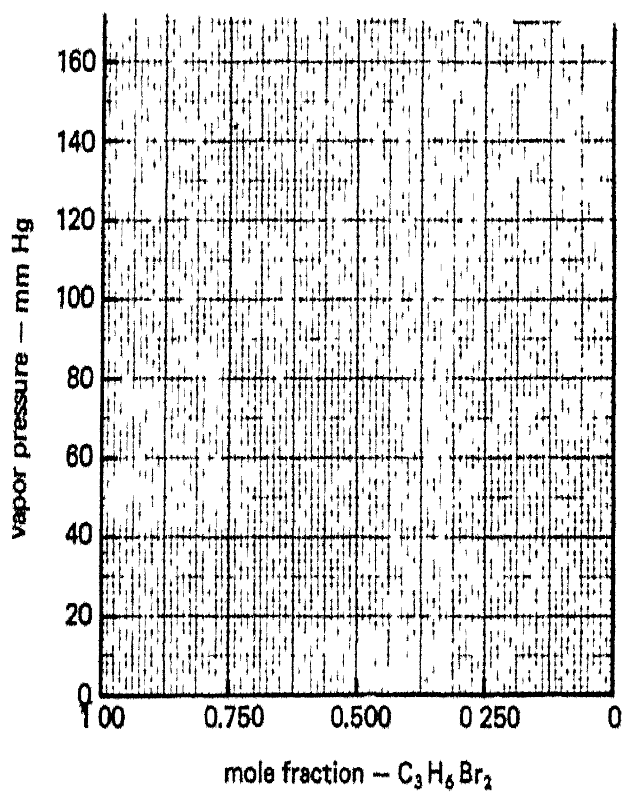
c) $X_{C_3H_6Br_2} = 0.750$

A-14 a) $P_{C_3H_6Br_2} = (0.250)(130 \text{ mm Hg})$
$= 32.5 \text{ mm Hg}$

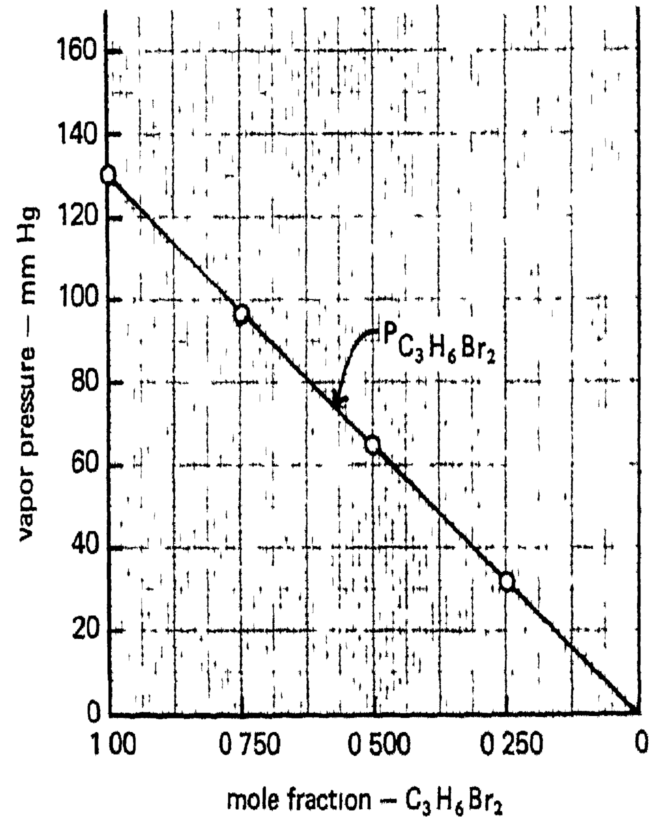
b) $P_{C_3H_6Br_2} = (0.500)(130 \text{ mm Hg})$
$= 65.0 \text{ mm Hg}$

c) $P_{C_3H_6Br_2} = (0.750)(130 \text{ mm Hg})$
$= 97.5 \text{ mm Hg}$

Q-15 Plot the values for the vapor pressure of $C_3H_6Br_2$ calculated in A-14 on the figure below.



A-15



S-3 For an ideal solution of two or more volatile liquids the total vapor pressure is equal to the sum of the partial pressures of all the components.

Q-16 Consider an ideal solution with the mole fraction of ethylene dibromide, $C_2H_4Br_2$, equal to 0.250 and the mole fraction of propylene dibromide, $C_3H_6Br_2$, equal to 0.750. What is the total vapor pressure of this solution at 85° C? (See A-11 and A-14 for partial pressure data.)

A-16 $P_{total} = P_{C_2H_4Br_2} + P_{C_3H_6Br_2}$
$= 42.5\text{ mm} + 97.5\text{ mm}$
$= 140\text{ mm}$

Q-17 Calculate the total vapor pressure of the following solutions at 85°C, assuming ideal behavior:

a) $X_{C_2H_4Br_2} = 0.500$
$X_{C_3H_6Br_2} = 0.500$

b) $X_{C_2H_4Br_2} = 0.750$
$X_{C_3H_6Br_2} = 0.250$

(See A-12 and A-14.)

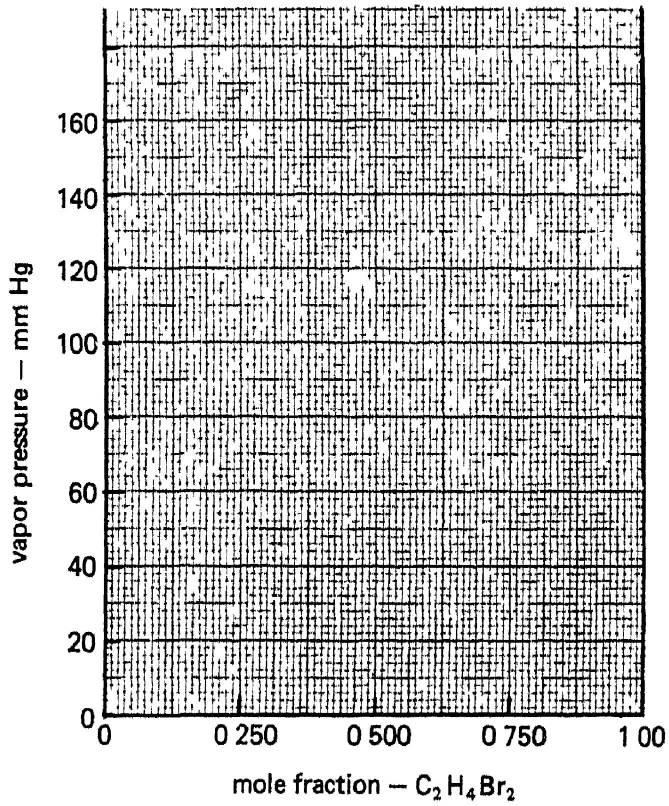
A-17 a) $P_{total} = 85.0\ mm + 65.0\ mm$

$= 150\ mm$

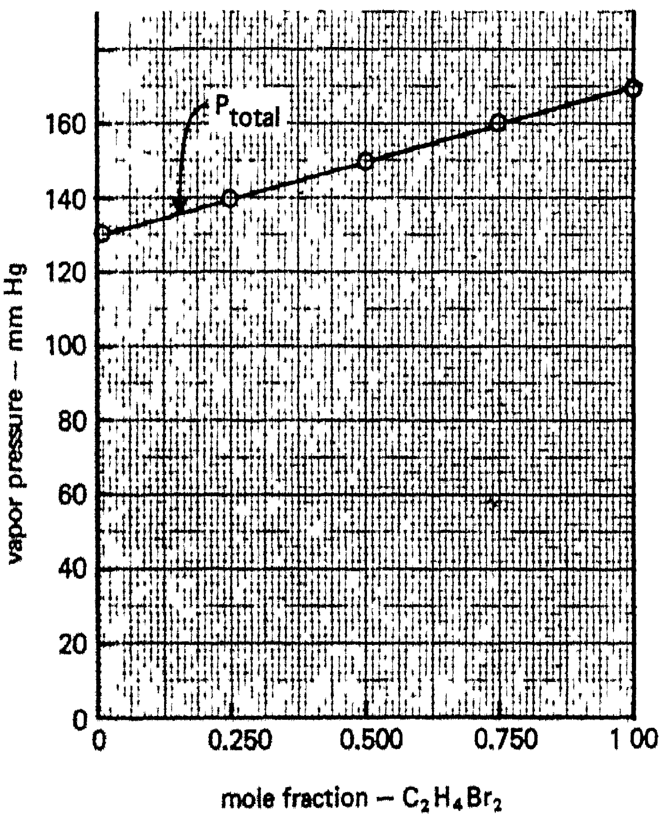
b) $P_{total} = 128\ mm + 32.5\ mm$

$= 160\ mm$

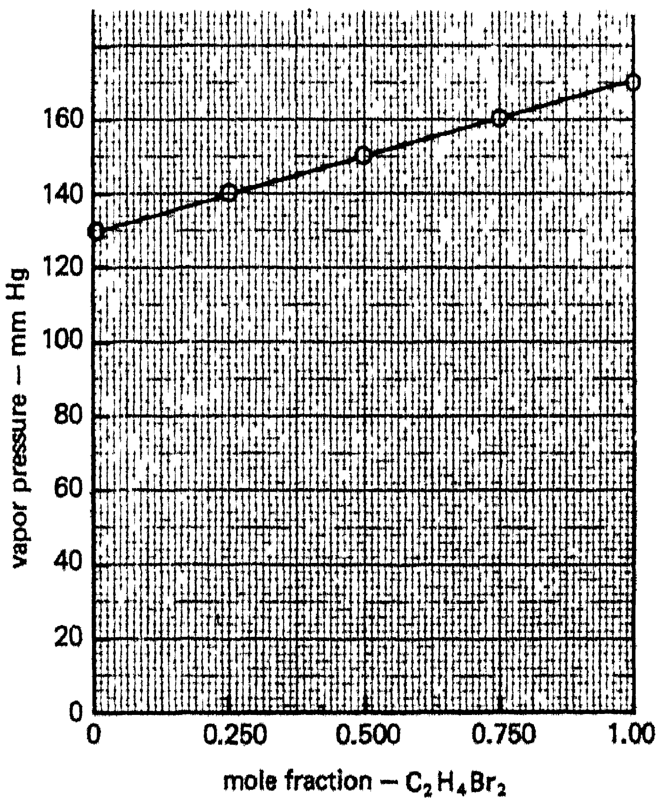
Q-18 Plot the values for total vapor pressure calculated in A-16 and A-17 on the figure below.



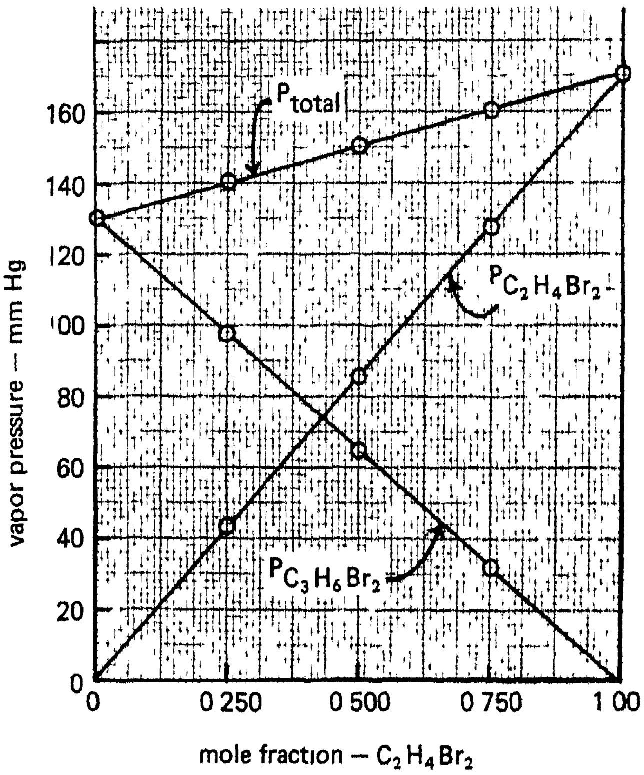
A-18



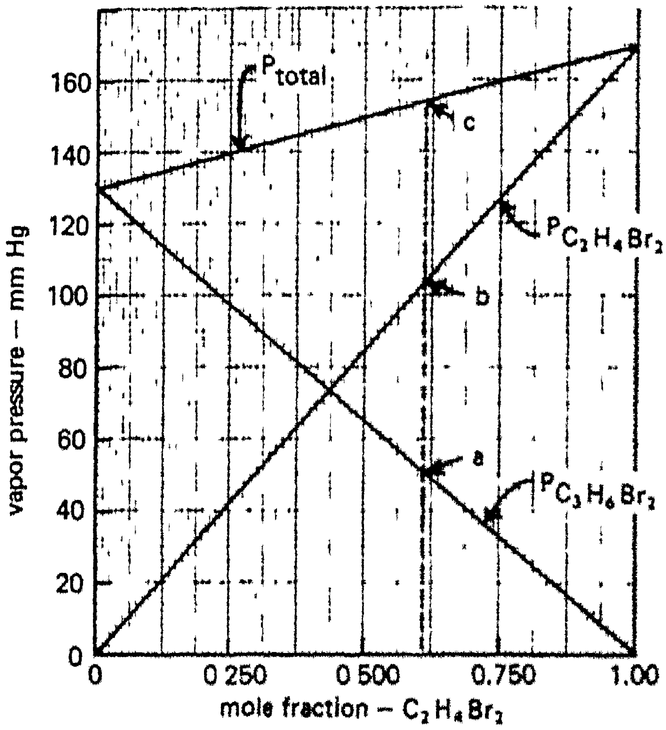
Q-19 Refer to A-13 and A-15 and plot the values for the partial pressure of ethylene dibromide and propylene dibromide on the figure below.



A-19



Q-20 The figure in A-19 is a graphical representation of the fact that the total vapor pressure of volatile liquids in an ideal solution is equal to the sum of the partial pressures. To verify this, determine the value of the vapor pressure at points a, b, c on the figure below.



A-20 point a pressure = 50.0 mm

point b pressure = 105 mm

point c pressure = 155 mm

Q-21 Calculate the total vapor pressure for the following solution at 20°C, assuming ideal behavior.

$$X_{C_6H_6} = 0.250$$
$$X_{CH_3C_6H_5} = 0.750$$
$$P^\circ_{C_6H_6} = 74.2 \text{ mm Hg } (20^\circ C)$$
$$P^\circ_{CH_3C_6H_5} = 20.9 \text{ mm Hg } (20^\circ C)$$

A-21
$$\begin{aligned} P_{benzene} &= P^\circ_{benzene} X_{benzene} \\ &= (74.2 \text{ mm})(0.250) \\ &= 18.6 \text{ mm} \end{aligned}$$
$$\begin{aligned} P_{toluene} &= P^\circ_{toluene} X_{toluene} \\ &= (20.9 \text{ mm})(0.750) \\ &= 15.7 \text{ mm} \end{aligned}$$
$$\begin{aligned} P_{total} &= P_{benzene} + P_{toluene} \\ &= 18.6 \text{ mm} + 15.7 \text{ mm} \\ &= \underline{34.3 \text{ mm}} \end{aligned}$$

Q-22 **Calculate the total vapor pressure of the following solution at 20°C.**

$$X_{C_6H_6} = 0.500$$
$$X_{CH_3C_6H_5} = 0.500$$

Assume ideal behavior.

A-22 $P_{benzene} = (74.2\ mm)(0.500)$
$= 37.1\ mm$
$P_{toluene} = (20.9\ mm)(0.500)$
$= 10.4\ mm$
$P_{total} = 37.1\ mm + 10.4\ mm$
$= \underline{47.5\ mm}$

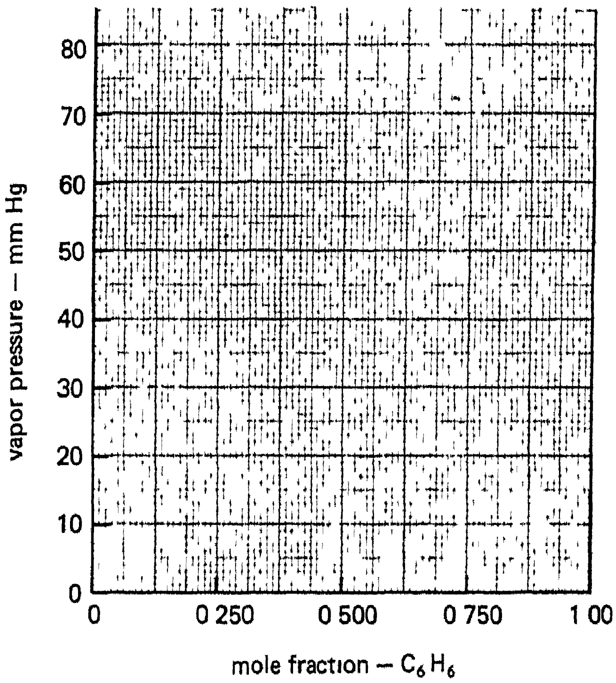
Q-23 Calculate the total vapor pressure of the following solution at 20°C.

$X_{C_6H_6} = 0.750$
$X_{CH_3C_6H_5} = 0.250$

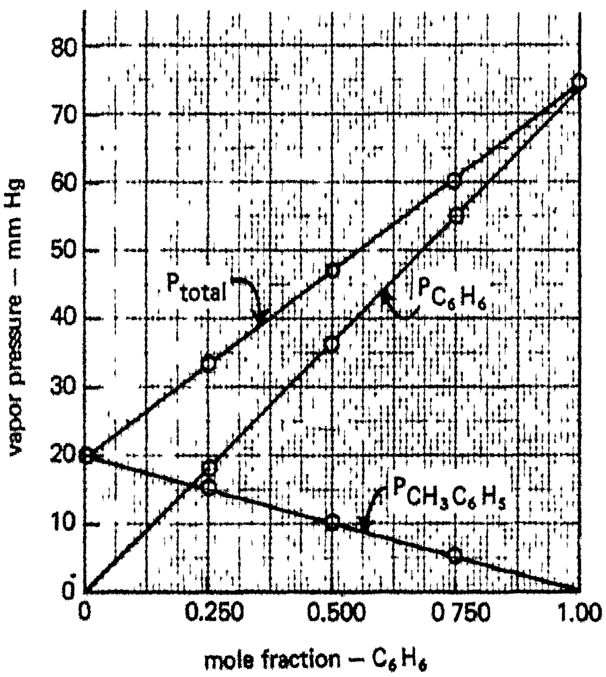
Assume ideal behavior

A-23 $P_{benzene} = (74.2\ mm)(0.750)$
$= 55.6\ mm$
$P_{toluene} = (20.9\ mm)(0.250)$
$= 5.22\ mm$
$P_{total} = \underline{60.8\ mm}$

Q-24 Plot the values for partial and total pressure calculated in A-21, A-22 and A-23 on the figure below.



A-24



[redacted]

S-4 The vapor pressure exerted by a solution of two liquids is due to the bombardment of the walls of the container by the vapor molecules The vapor is a mixture composed of molecules from both components of the solution For an ideal solution the vapor composition can be calculated

Q-25 How is the pressure of a vapor related to the number of molecules of a gas present?

A-25 The pressure of a gas is directly proportional to the number of molecules

Q-26 How is the partial pressure of a gas, P_A, related to the number of moles of a gas, n_A^{vapor}, present in a mixture of gases? Express the answer in equation form.

A-26 The partial pressure is directly proportional to the number of moles of gas present in a mixture of gases.

$P_A = k\,n_A^{vapor}$ where P_A is the partial pressure, k is a proportionality constant which is the same for all gases, and n_A^{vapor} are the moles of gas a.

Q-27 Write an equation in terms of n_A^{vapor} and n_B^{vapor} for the mole fraction of a gas, X_A^{vapor}, in a mixture of two gases A and B

A-27

$$X_A^{vapor} = \frac{n_A^{vapor}}{n_A^{vapor} + n_B^{vapor}}$$

Q-28 Write an equation which shows the relationship of the mole fraction of a gas, X_A^v, ($X_A^v = X_A^{vapor}$) to the partial pressure of A and B in a mixture of the two gases.

(Hint: Refer to A-26 and A-27.)

A-28

$$X_A^v = \frac{n_A^v}{n_A^v + n_B^v}$$

$P_A = k\,n_A^v \qquad P_B = k\,n_B^v$

Therefore,

$$X_A^v = \frac{P_A/k}{P_A/k + P_B/k}$$

and

$$X_A^v = \frac{P_A}{P_A + P_B} = \frac{P_A}{P_{total}}$$

Q-29 Remembering that $X_A^v = \dfrac{P_A}{P_{total}}$ and that $P_A = X_A^{\ell} P_A^{\circ}$, ($X_A^{\ell} = X_A^{liquid}$) write an equation which shows the relationship of the mole fraction of vapor to the mole fraction of liquid and the vapor pressure of the pure liquid.

A-29 $P_A = X_A^{\ell} P_A^{\circ}$

Thus,

$$X_A^v = \frac{X_A^{\ell} P_A^{\circ}}{P_{total}}$$

Q-30 Calculate the mole fraction of benzene in the vapor phase that is in equilibrium with the following solution at 20°C.

$X_{benzene}^{\ell} = 0.250$

$X_{toluene}^{\ell} = 0.750$

$P^{\circ}_{C_6H_6} = 74.2$ mm Hg (20°C)

$P_{total} = 34.2$ mm Hg (20°C)

Assume ideal behavior.

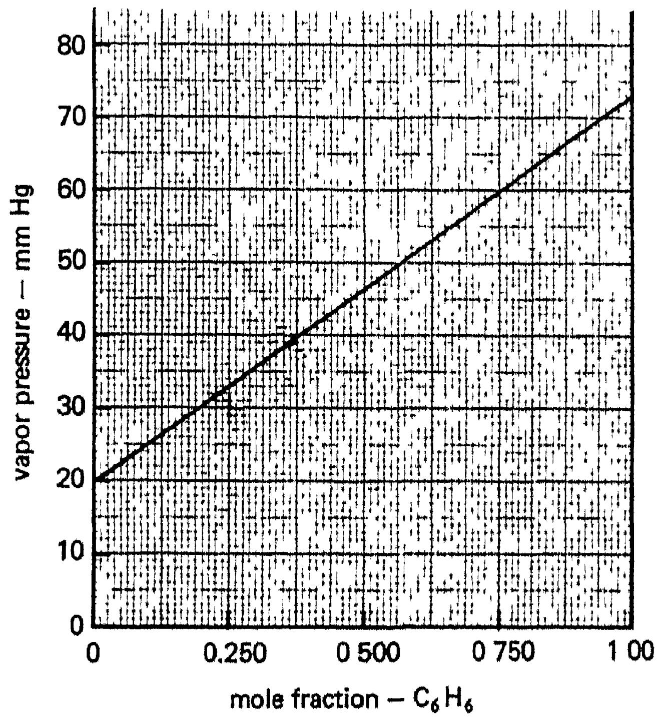
A-30

$$X_A^v = \frac{X_A^\ell P_A^\circ}{P_{total}}$$

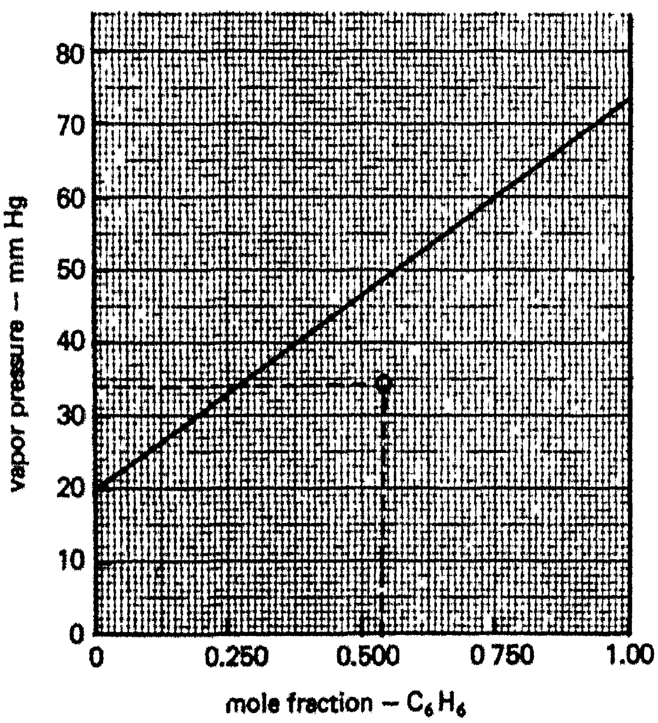
$$X_{C_6H_6}^v = \frac{(0.250)(74.2 \text{ mm})}{(34.2 \text{ mm})}$$

$$= 0.542$$

Q-31 The figure given below is a graph of the total vapor pressure as a function of mole fraction (plotted in A-24) for the benzene-toluene system. By using the same abscissa (x-axis) to represent the composition of the vapor as well as the liquid composition, plot on the graph the value of the mole fraction of benzene vapor at the total vapor pressure given in Q-30.



A-31 The total vapor pressure for the solution is 34.2 mm (see A-30).



Q-32 Calculate the mole fraction of benzene in the vapor phase that is in equilibrium with the following solution at 20° C.

$X_{benzene}^\ell = 0.500$

$X_{toluene}^\ell = 0.500$

$P_{total} = 47.5$ mm Hg (20° C)

Assume ideal behavior.

A-32

$$X^{V}_{C_6H_6} = \frac{X^{\ell}_{C_6H_6}\, P^{\circ}_{C_6H_6}}{P_{total}}$$

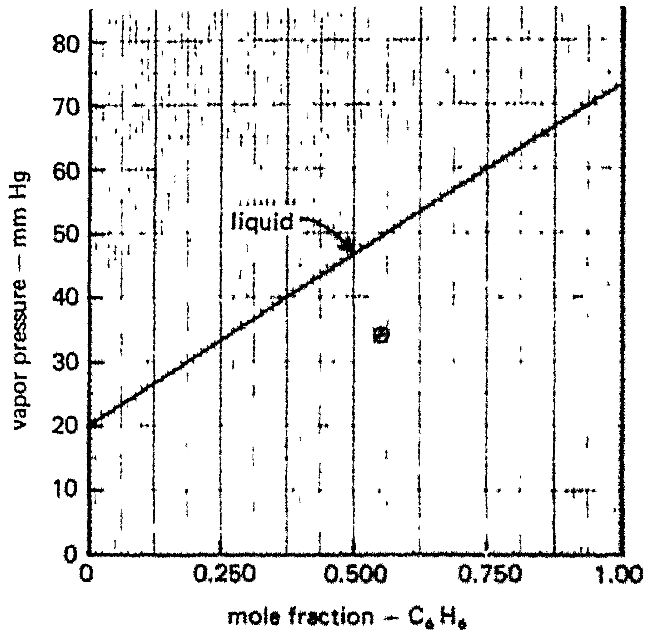
$$= \frac{(0\ 500)(74.2\ \text{mm})}{(47.5\ \text{mm})}$$

$$= 0.781$$

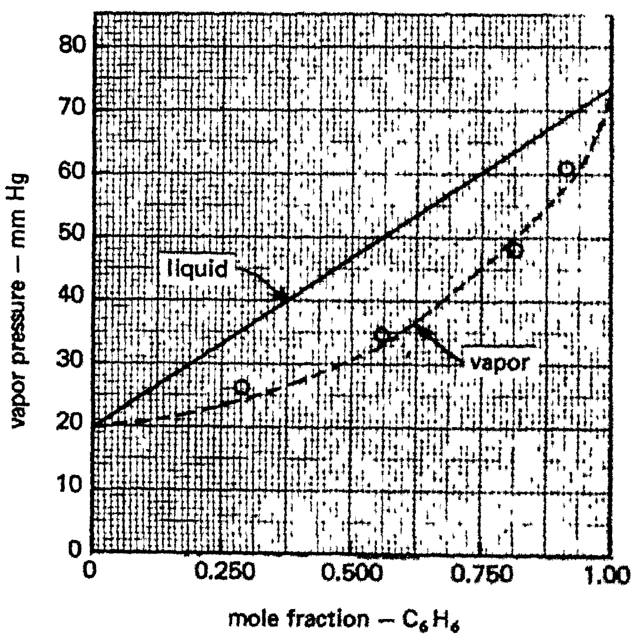
Q-33 The following data give the mole fraction of benzene in the vapor phase for two more solutions at 20°C:

$X^{\ell}_{benzene}$	$X^{\ell}_{toluene}$	$X^{V}_{C_6H_6}$	P_{total}
0.750	0.250	0.912	60.8 mm
0.100	0.900	0 283	26.2 mm

Plot on the graph below the value obtained in A-32 and the data given above



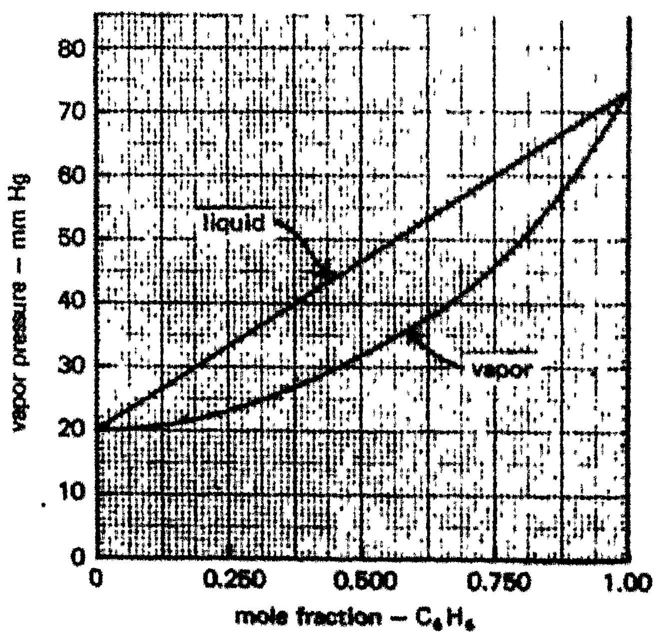
A-33



Q-34 The graph obtained in A-33 (shown below) can be used to determine the vapor composition above any solution of benzene and toluene.

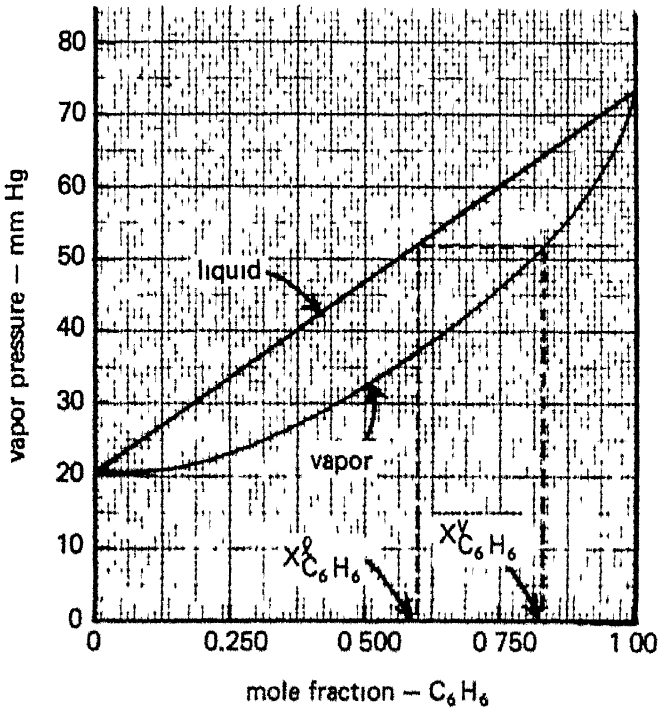
What is the composition of vapor in equilibrium with the following solution?

$X^{\ell}_{C_6H_6} = 0.600 \quad X^{\ell}_{CH_3C_6H_5} = 0.400$



A-34 The graph shows that

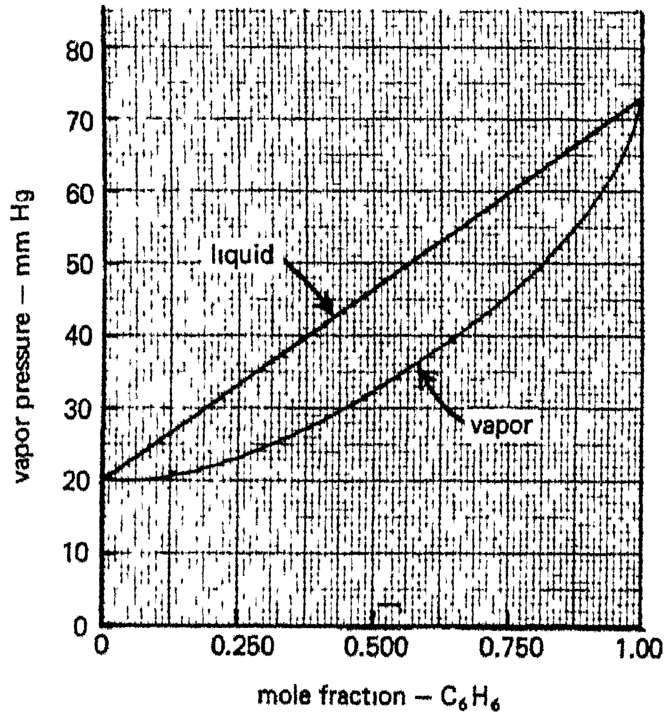
$X^{v}_{C_6H_6} = 0.83 \qquad X^{v}_{CH_3C_6H_5} = 0.17$



Q-35 According to the graph obtained in A-33 (shown below) what is the composition of the vapor in equilibrium with the following solution?

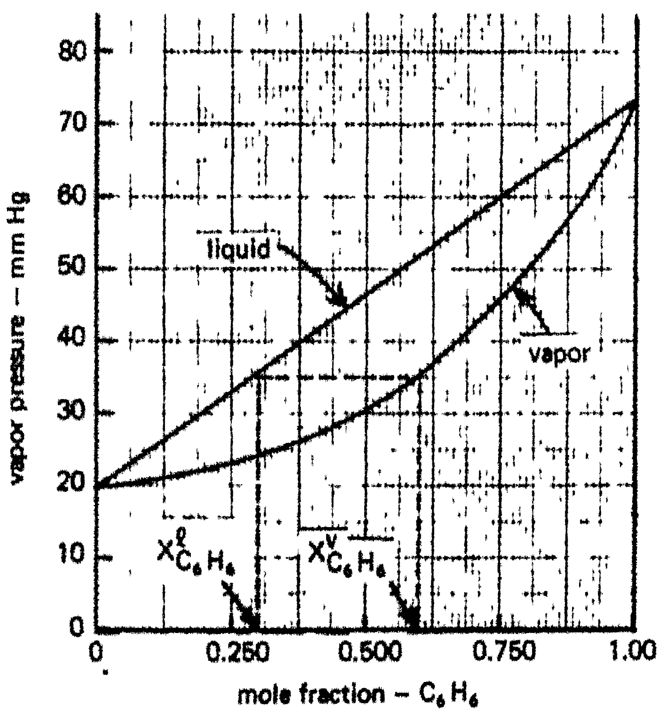
$X^{\ell}_{C_6H_6} = 0.300$

$X^{\ell}_{CH_3C_6H_5} = 0.700$

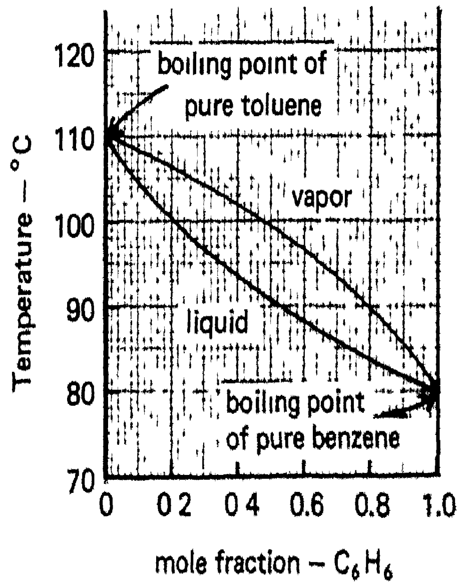


A-35 The graph shows that

$X^{v}_{C_6H_6} = 0.60 \qquad X^{v}_{CH_3C_6H_5} = 0.40$



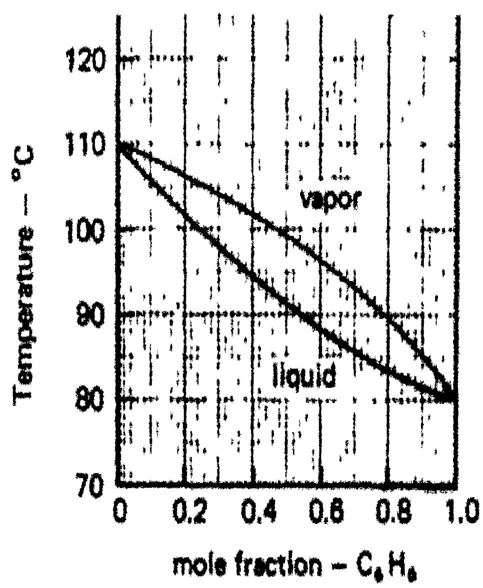
S-5 In the previous section, vapor pressure diagrams were studied. On these diagrams pressure was plotted versus mole fraction and temperature was constant. It is also useful to construct boiling point diagrams. On these diagrams, the temperature at which liquid and vapor are at equilibrium at one atmosphere (normal boiling point) is plotted versus mole fraction. The boiling point diagram shown below is for the nearly ideal benzene-toluene system.



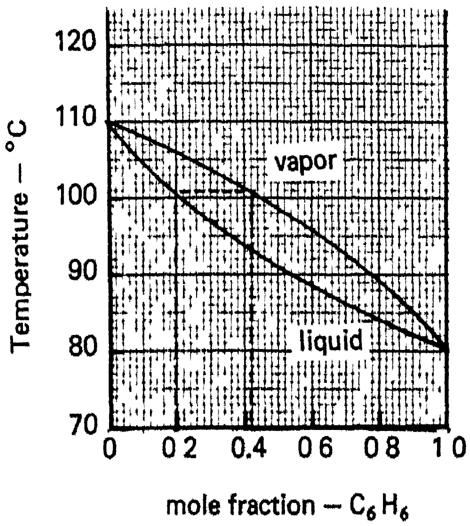
Q-36 What is the composition of the vapor in equilibrium with the following solution at its normal boiling point?

$$X^{\ell}_{C_6H_6} = 0.20$$

$$X^{\ell}_{CH_3C_6H_5} = 0.80$$



A-36



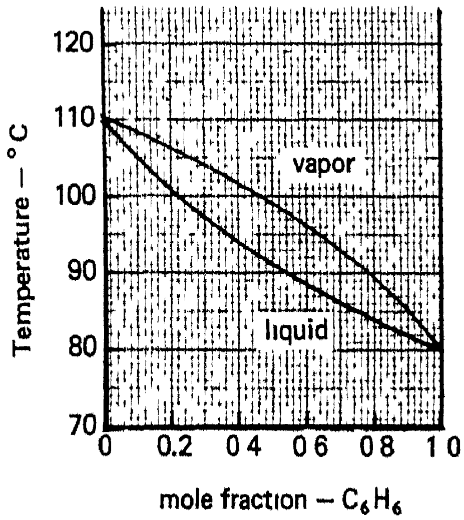
$X^{v}_{C_6H_5} = 0.42$

$X^{v}_{CH_3C_6H_5} = 0.58$

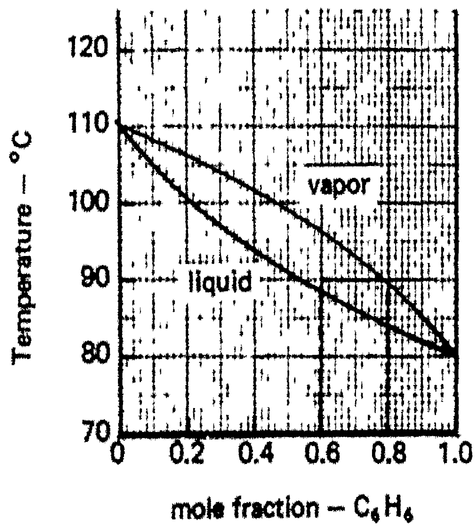
Q-37 What is the composition of the vapor in equilibrium with the following solution at its normal boiling point?

$X^{\ell}_{C_6H_6} = 0.60$

$X^{\ell}_{CH_3C_6H_5} = 0.40$



A-37



$X^{v}_{C_6H_6} = 0.80$

$X^{v}_{CH_3C_6H_5} = 0.20$

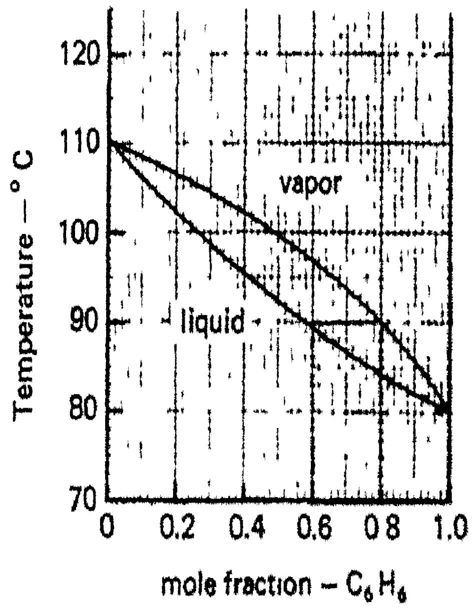
Q-38 How does the mole fraction of benzene vapor in equilibrium with the solution at its normal boiling point in Q-37 compare with the mole fraction of benzene in the solution?

A-38 The vapor has a higher mole fraction of benzene than the solution. (0.80 compared to 0.60.)

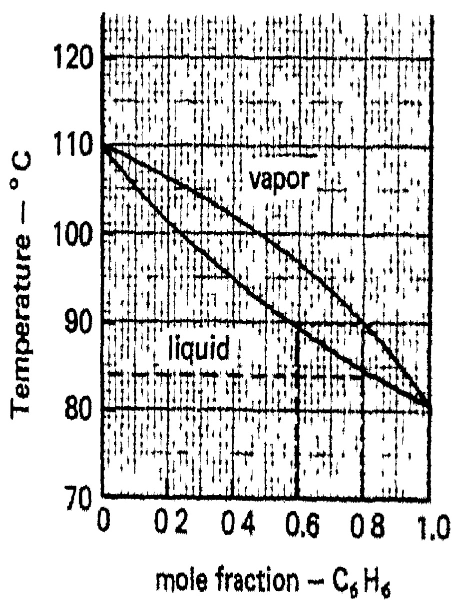
Q-39 A substance is said to be more volatile than another if it has a higher vapor pressure at any given temperature. Is benzene or toluene more volatile?

A-39 Benzene has a lower boiling point; therefore, it has a higher vapor pressure which causes it to be more volatile than toluene.

Q-40 In general, the vapor in equilibrium with a solution will always have a higher mole fraction of the more volatile component than did the original solution. If a portion of the vapor above the solution in Q-37 were removed from the system and cooled, at what temperature would it condense?

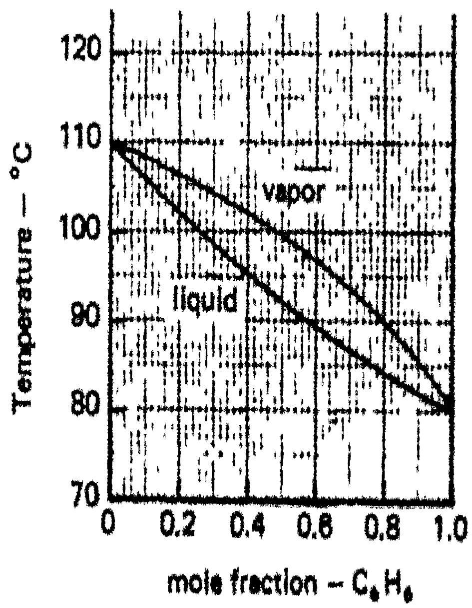


A-40

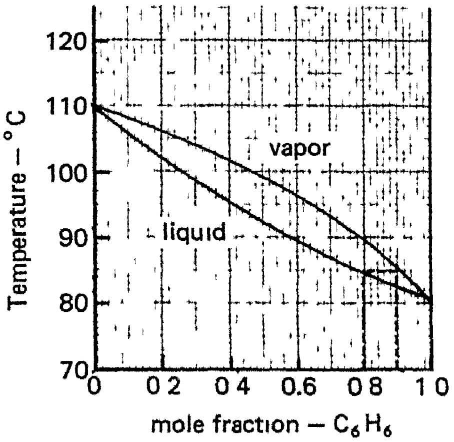


Condensation temperature = 84°C

Q-41 What would be the composition of the vapor in equilibrium with the liquid condensed in Q-40 if the liquid is at its normal boiling point?



A-41

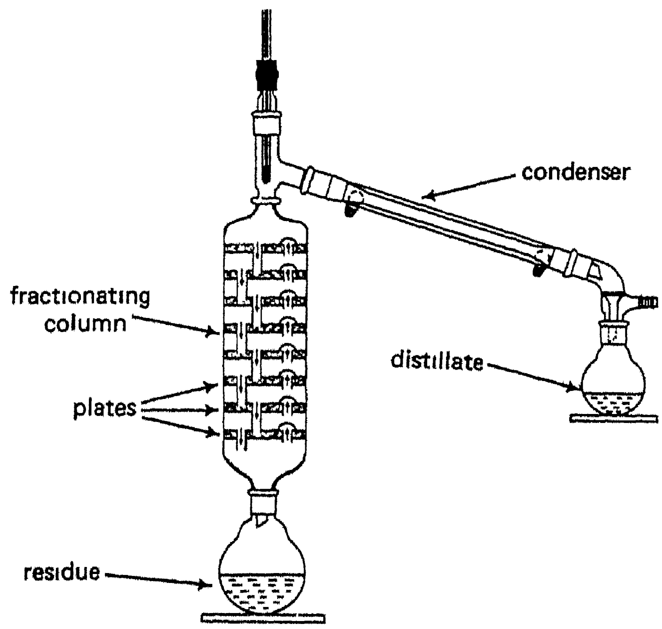


$X^{v}_{C_6H_6} = 0.90$

$X^{v}_{CH_3C_6H_5} = 0.10$

Q-42 The process of condensation and vaporization can be repeated over and over (fractional distillation) by means of a fractionating column which is illustrated below. At each plate, condensation occurs and the liquid and vapor are re-equilibrated. The mole fraction of the more volatile component continuously increases in the portion condensed (distillate) on each successive plate

What happens to the composition of the residue?



A-42 The residue is enriched in the less volatile component.

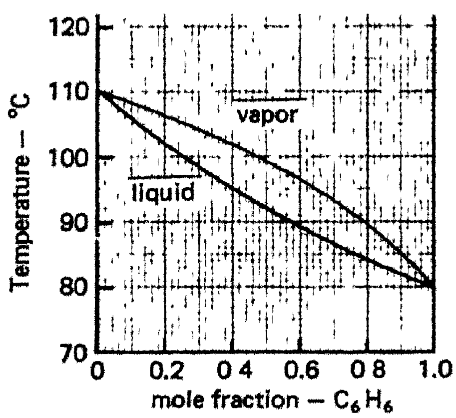
Q-43 How does the boiling point of the residue compare with that of the original solution?

A-43 The normal boiling point of the residue would increase because more high boiling component is present.

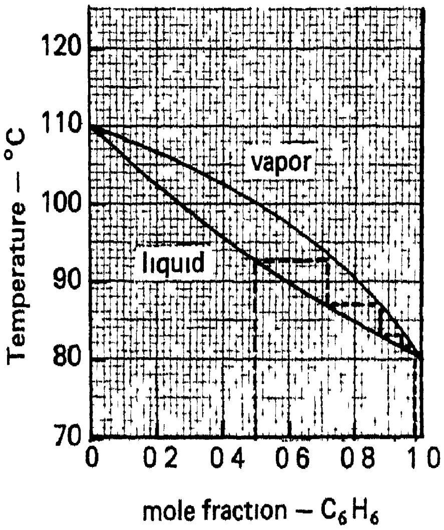
Q-44 In order to verify that benzene and toluene can be separated by fractional distillation, sketch on the curve below four fractional distillation steps starting with the following solution.

$X^{\ell}_{C_6H_6} = 0.5 \qquad X^{\ell}_{CH_3C_6H_5} = 0.5$

What is the vapor composition after four distillation steps?



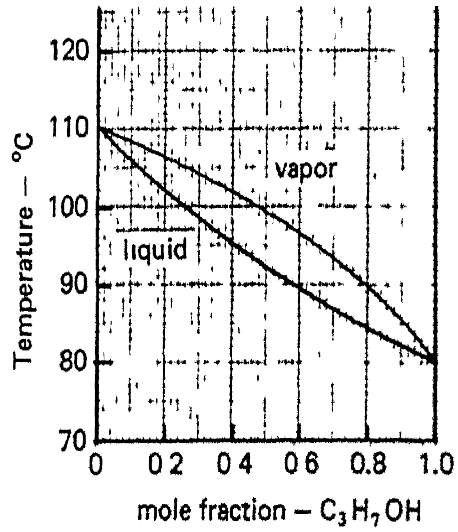
A-44



$X^v_{C_6H_6} = 0.98$

$X^v_{CH_3C_6H_5} = 0\ 02$

Q-45 The diagram below is the boiling point diagram for the nearly ideal system 2-methyl propanol-1 (C_4H_9OH) and propanol-2 (C_3H_7OH)

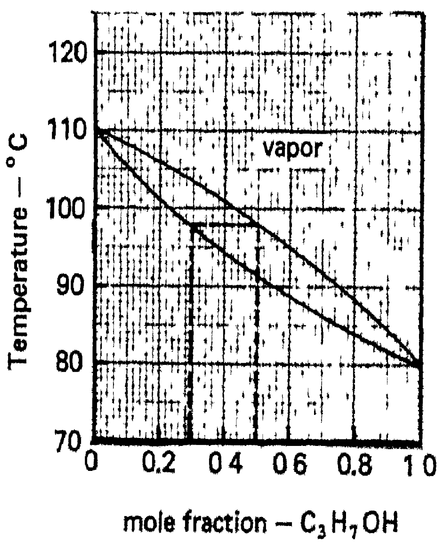


What is the composition of the vapor in equilibrium with the following solution at its normal boiling point?

$X^\ell_{C_3H_7OH} = 0.30$

$X^\ell_{C_4H_9OH} = 0.70$

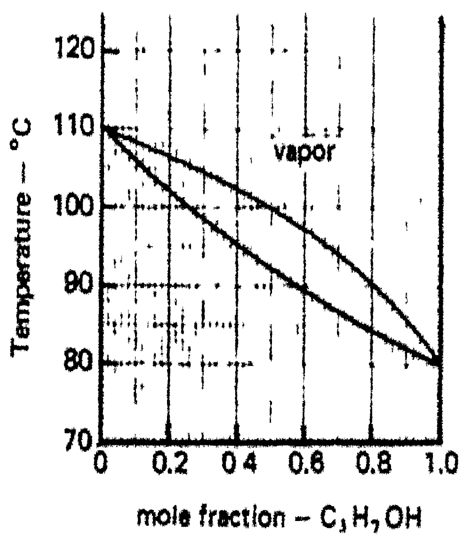
A-45



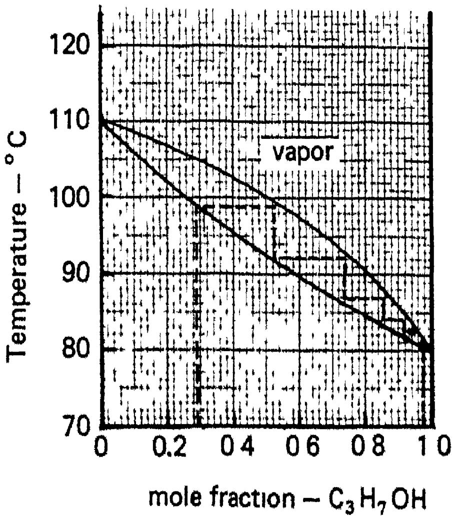
$X^v_{C_3H_7OH} = 0.5$

$X^v_{C_4H_9OH} = 0.5$

Q-46 What would be the composition of the distillate from the solution in Q-45 after five fractional distillation steps?



A-46



$X^{V}_{C_3H_7OH} = 0.98$

$X^{V}_{C_4H_9OH} = 0.02$

Q-47 What change would occur in the composition and boiling point of the residue during the fractional distillation described in Q-46?

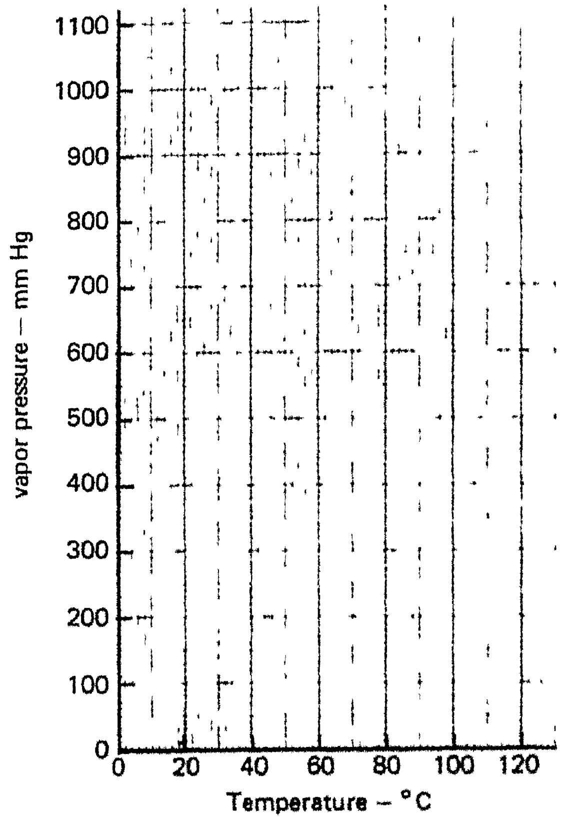
A-47 The residue would be continuously enriched in the higher boiling component (C_4H_9OH) and its boiling point would increase.

PART II: Solutions of Nonvolative Solutes

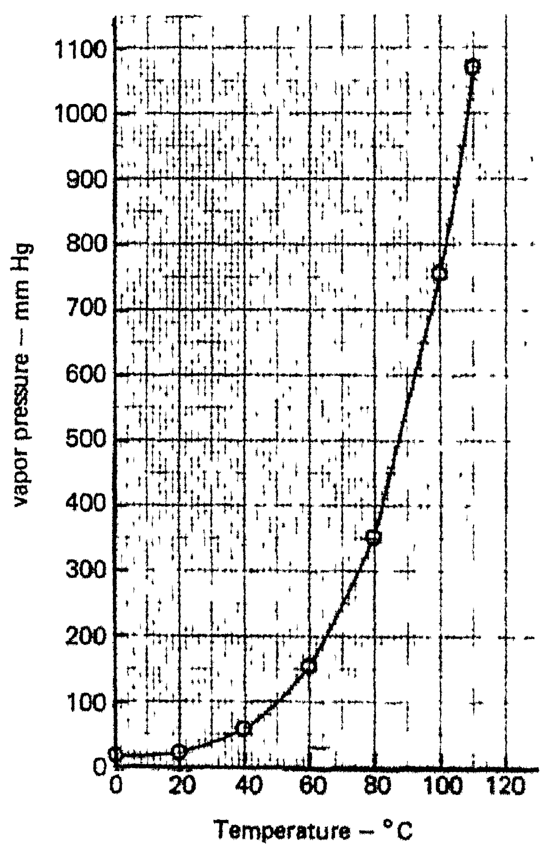
S-1 The vapor pressure of a pure liquid depends on temperature. The following data give the vapor pressure of water at various temperatures from zero to 110°C.

Temperature °C	Pressure - mm Hg
0	4.6
20	17.5
40	55.3
60	149
80	355
100	760
110	1074

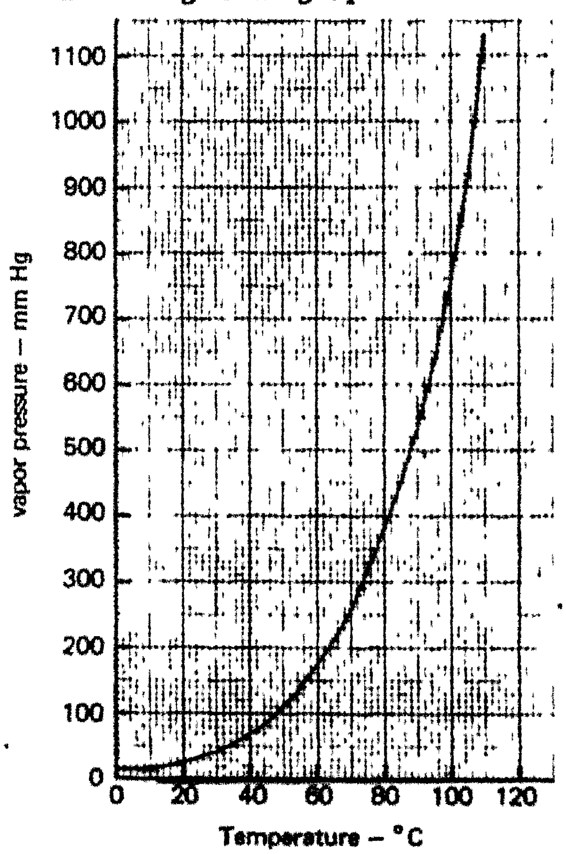
Q-1 Using the figure below, plot the data given for water in S-1, and draw a smooth curve to represent the dependence of the vapor pressure of water on temperature.



A-1

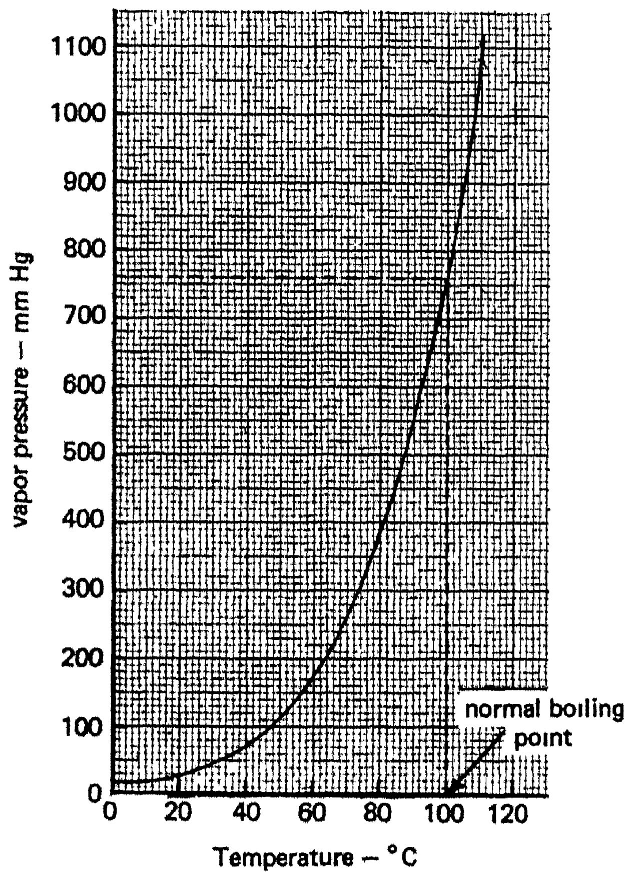


Q-2 What is the definition of the normal boiling point of a pure liquid? What is the normal boiling point of pure water according to the graph below.



A-2 The normal boiling point of a pure liquid is the temperature at which the vapor pressure is equal to one atmosphere or 760 mm Hg

The normal boiling point of pure water is 100°C.



Q-3 If a nonvolatile solute is dissolved in a pure liquid, it is observed that the vapor pressure is lowered. Explain this phenomenon in terms of Raoult's law.

(Hint A nonvolatile solute by definition would not contribute to the total vapor pressure.)

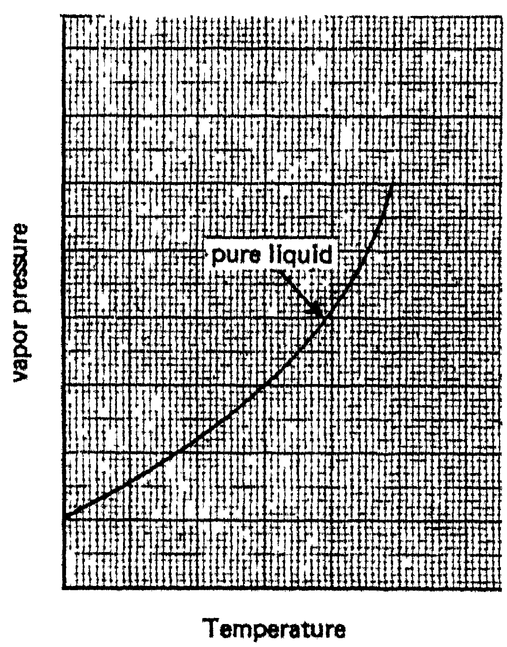
A-3 Since the solute does not contribute to the total vapor pressure, the total vapor pressure is equal to the partial pressure of the solvent.

Raoult's law says

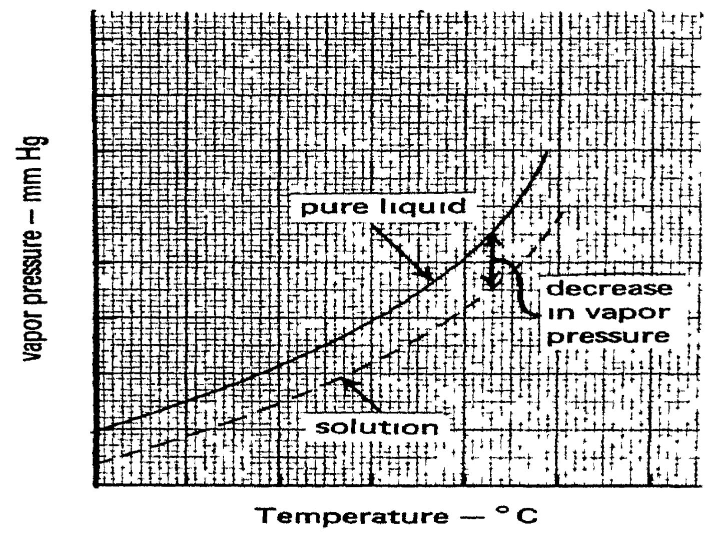
$$P_A = P^\circ_A X^\ell_A$$

Since X^ℓ_A is always less than one for a solution, the partial pressure, P_A, is always less than the pressure of the pure liquid P°_A.

Q-4 Below is a plot of vapor pressure vs temperature for a pure liquid. A nonvolatile solute is added to the liquid. Sketch the vapor pressure - temperature curve for the resulting solution.

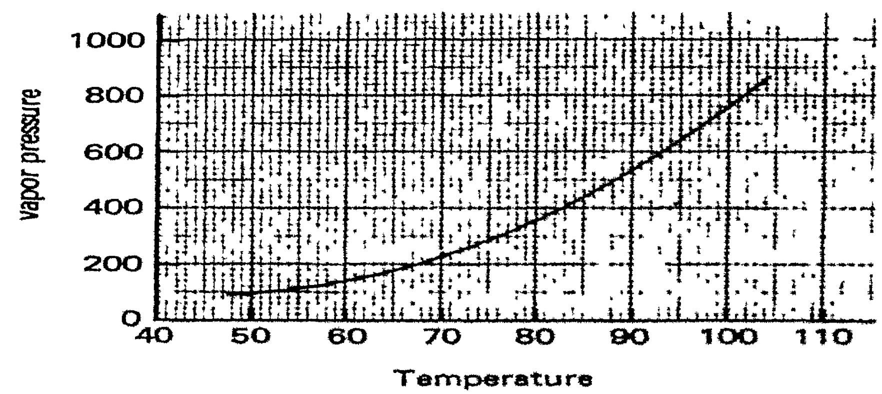


A-4

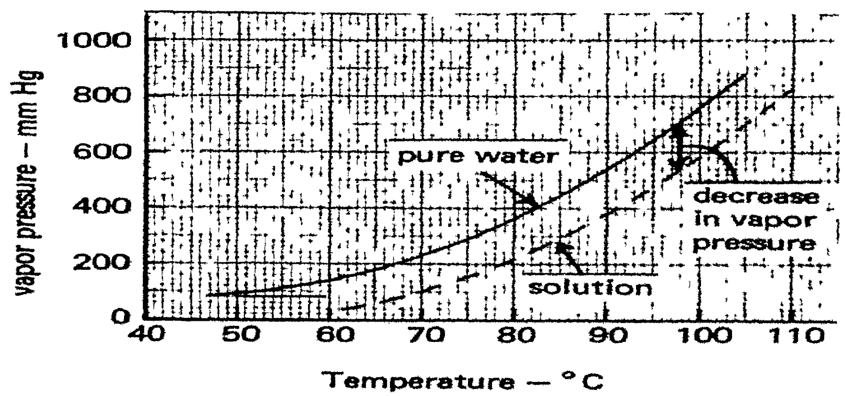


Q-5 Vapor pressure lowering is a colligative property, i.e., it is a property which depends only on the number of solute particles in solution and not on the nature of these particles.

The following figure shows the vapor pressure curve for water. Sketch the vapor pressure after addition of a non-volatile solute.



A-5



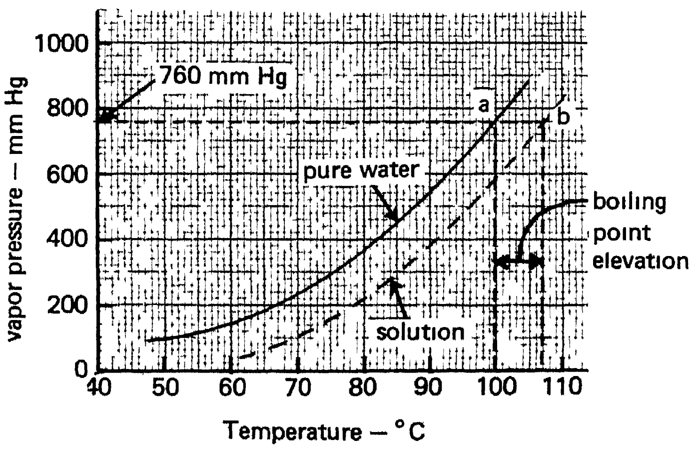
Q-6 Will the normal boiling point of an aqueous solution and of pure water be the same? Why?

A-6 Since the vapor pressure of the pure liquid and the solution are different, the normal boiling point of the two will be different.

Q-7 Will the normal boiling point of an aqueous solution be higher or lower than the normal boiling point of the pure solvent.

(Hint: Refer to the figure in A-5.)

A-7



The boiling point of a solution is higher because the temperature at which the vapor pressure equals 760 mm is higher (point b)

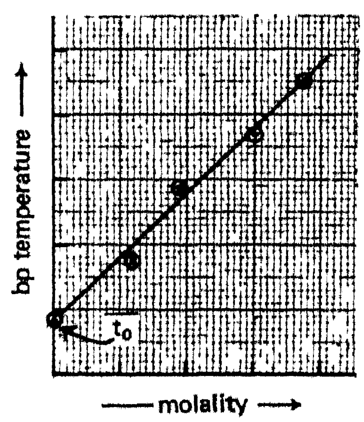
Q-8 The boiling point elevation is a colligative property, i.e., it is a property which depends only on the number of solute particles in solution and not on the nature of these particles. The concentration unit most useful in expressing the number of solute particles when dealing with colligative properties is molality. What is the definition of molality?

A-8 Molality is the moles of solute per kg (1000 g) of solvent.

Q-9 If one mole of solute particles is dissolved in 1000 g of pure solvent, the boiling point elevation is always the same and is characteristic of the solvent. This change in boiling point is called the molal boiling point elevation constant, K_b. K_b is different for different solvents. For water, K_b is observed to be 0.52 °C. If one mole of a sugar is dissolved in 1000 g of water, what is the boiling point of the resulting solution?

A-9 $T_b = 100.00°C + 0.52°C$
$= 100.52°C$

Q-10 Below is a plot of boiling point vs the molal concentration for a series of dilute solutions.



The slope of the line is equal to K_b, the molal boiling point constant. The point t_0 is the boiling point of the pure solvent.

a) Derive an equation which relates the boiling point of a solution, t, molality, m, the constant K_b, and the boiling point of the pure solvent, t_0.
b) Derive an equation for the boiling point elevation $(t - t_0)$.

A-10 The equation of a straight line has the form:

$$y = ax + b$$

In the plot, $y = t$, $a = K_b$, $x = m$, and $b = t_0$

Therefore

$$t = K_b m + t_0$$

$$t - t_0 = \Delta T = K_b m$$

Q-11 If 2 0 moles of a sugar are dissolved in 1000 g of water, what is the boiling point of the resulting solution?

(Assume that the solute is nonvolatile.)

A-11 $\Delta T = K_b m$

$= (0.52\ \text{deg}/\cancel{\text{molal}})(2\ 0\ \cancel{\text{molal}})$

$= 1.0°\text{C}$

$T_b = 100.00 + 1.0 = 101\ 0°\text{C}$

Q-12 If 2.0 moles of a sugar are dissolved in 500 g of water, what is the boiling point of the resulting solution?

A-12 $\dfrac{2\ 0\ \text{mole}}{500\ \cancel{\text{g}}} \cdot \dfrac{1000\ \cancel{\text{g}}}{1\ \text{kg}} = \dfrac{4.0\ \text{mole}}{\text{kg}}$

$= 4.0$ molal

$\Delta T = K_b m$

$= \dfrac{0\ 52\ \text{deg}}{\cancel{\text{molal}}} \cdot 4.0\ \cancel{\text{molal}}$

$= 2.1$ deg

$T_b = 100.00°\text{C} + 2.1°\text{C}$

$= 102.1°\text{C}$

Q-13 The molal boiling point elevation constant (K_b) for CCl_4 is 5.02 deg/mole. The boiling point of pure CCl_4 is 76.8°C. Calculate the boiling point of a 1.00 molal solution of naphthalene, $C_{10}H_8$, in CCl_4

(Assume that the solute is nonvolatile.)

A-13 $\Delta T = K_b m$

$= \dfrac{5\ 02\ \text{deg}}{\cancel{\text{molal}}} \cdot 1.00\ \cancel{\text{molal}}$

$= 5.02$ deg

$T_b = (76.8 + 5.02)°\text{C}$

$= 81.8°\text{C}$

Q-14 What is the boiling point of a solution made by dissolving 2.00 g of naphthalene, $C_{10}H_8$, in 25.0 g of CCl_4?

A-14 $K_b = 5.02$ deg/molal

$m = \dfrac{2.00\ \cancel{\text{g } C_{10}H_8}}{25.0\ \cancel{\text{g } CCl_4}} \cdot \dfrac{1000\ \cancel{\text{g } CCl_4}}{1\ \text{kg } CCl_4} \cdot \dfrac{1\ \text{mole } C_{10}H_8}{128\ \cancel{\text{g } C_{10}H_8}}$

$= 0.625\ \dfrac{\text{mole } C_{10}H_8}{1\ \text{kg } CCl_4} = 0.625$ molal

$\Delta T = \dfrac{5.02\ \text{deg}}{\cancel{\text{molal}}} \cdot 0.625\ \cancel{\text{molal}} = 3.14°\text{C}$

$T_b = (76.8 + 3.14)°\text{C} = 79.9°\text{C}$

Q-15 The boiling point elevation constant (K_b) for benzene, C_6H_6, is 2.57 deg/molal. The boiling point of pure benzene is 80.1°C. Calculate the boiling point of a solution made by dissolving 5.00 g of stilbene, $C_{14}H_{12}$, in 15.0 g of benzene.

(Assume that the solute is nonvolatile.)

A-15 $K_b = 2\ 57\ \text{deg/molal}$

$$m = \frac{5\ 00\ \cancel{g\ C_{14}H_{12}}}{15\ 0\ \cancel{g\ C_6H_6}} \left| \frac{1000\ \cancel{g\ C_6H_6}}{1\ kg\ C_6H_6} \right| \frac{1\ mole\ C_{14}H_{12}}{180\ \cancel{g\ C_{14}H_{12}}}$$

$$= 1\ 85\ \frac{mole\ C_{14}H_{12}}{1\ kg\ C_6H_6} = 1\ 85\ molal$$

$$\Delta T = \frac{2\ 57\ deg}{\cancel{molal}} \left| \frac{1\ 85\ \cancel{molal}}{} \right. = 4\ 75\ deg$$

$$T_b = (80\ 1 + 4\ 75)\ C = 84\ 8°C$$

Q-16 Calculate the value of K_b for chloroform, $CHCl_3$, from the following data

Boiling point of pure $CHCl_3$ = 61 3°C
A solution containing 5 02 g of napthalene, $C_{10}H_8$, in 18 0 g of $CHCl_3$ boils at 69 5°C.

A-16 $\Delta T = K_b m$

$$K_b = \frac{\Delta T}{m}$$

$$\Delta T = (69.5 - 61\ 3)°C = 8.2°C$$

$$m = \frac{5\ 02\ \cancel{g\ C_{10}H_8}}{18\ 0\ \cancel{g\ CHCl_3}} \left| \frac{1000\ \cancel{g\ CHCl_3}}{1\ kg\ CHCl_3} \right| \frac{1\ mole\ C_{10}H_8}{128\ \cancel{g\ C_{10}H_8}}$$

$$= \frac{2\ 18\ mole\ C_{10}H_8}{1\ kg\ CHCl_3} = 2\ 18\ molal$$

$$K_b = \frac{8.2\ deg}{2\ 18\ molal} = 3.8\ \frac{deg}{molal}$$

Q-17 Calculate the value of K_b for diethyl ether, $C_4H_{10}O$, given the following data.

Boiling point of pure diethyl ether is 34.6°C A solution of 6 80 g of benzoic acid, C_6H_5COOH, in 20.0 g of diethyl ether boils at 40 6°C (Assume that the solute is nonvolatile)

A-17 $\Delta T = K_b m$

$$K_b = \frac{\Delta T}{m}$$

$$\Delta T = (40.6 - 34\ 6)°C = 6.0°C$$

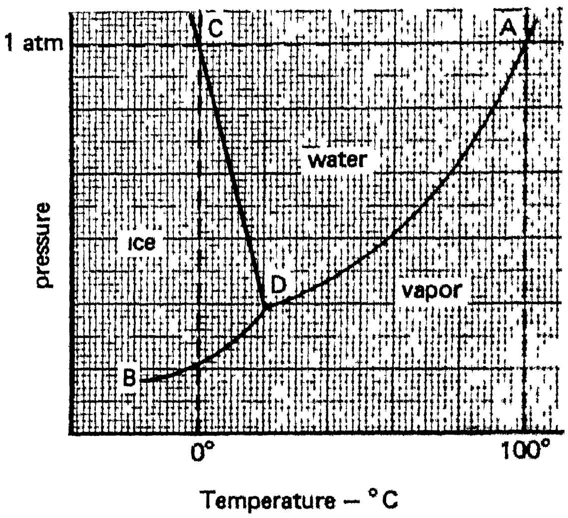
$$m = \frac{6\ 80\ \cancel{g\ C_6H_5COOH}}{20.0\ \cancel{g\ C_4H_{10}O}} \left| \frac{1000\ \cancel{g\ C_4H_{10}O}}{1\ kg\ C_4H_{10}O} \right| \frac{1\ mole\ C_6H_5COOH}{122\ \cancel{g\ C_6H_5COOH}}$$

$$= 2\ 79\ \frac{mole\ C_6H_5COOH}{1\ kg\ C_4H_{10}O} = 2.79\ molal$$

$$K_b = \frac{6.0\ deg}{2.79\ molal} = 2.2\ \frac{deg}{molal}$$

S-2 The figure below is a phase diagram for water (not drawn to scale). The line AD represents the temperatures and pressures at which water and its vapor are at equilibrium.

Line CD represents the temperatures and pressures at which water and ice are at equilibrium.
Line BD represents the temperatures and pressures at which ice and vapor are at equilibrium
Point D is the temperature and pressure at which ice, water and vapor are at equilibrium and is called the triple point.



Q-18 What point corresponds to the normal boiling point of pure water?

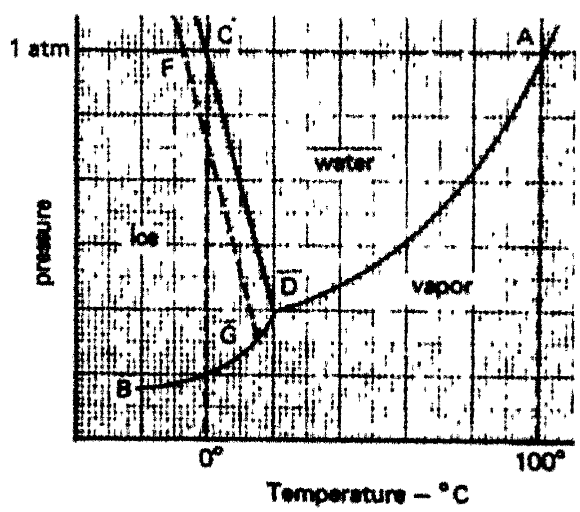
A-18 The boiling point at standard pressure is the temperature at which the vapor pressure equals 1 atmosphere. This corresponds to point A.

Q-19 What point corresponds to the freezing point of pure water at standard pressure?

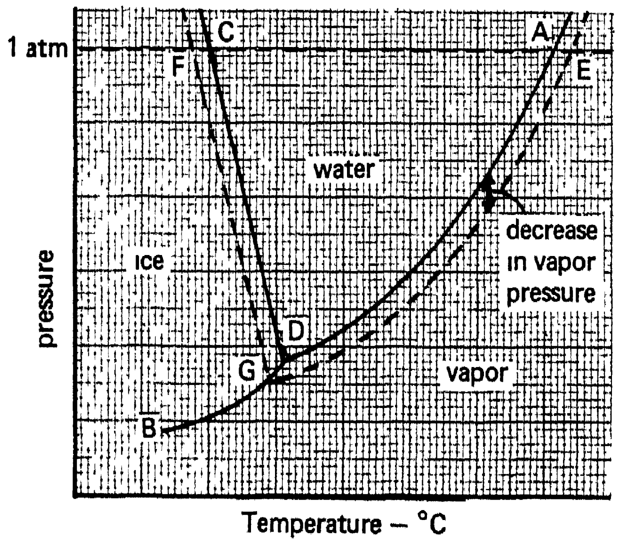
Q-19 The freezing point of a liquid at a given pressure is the temperature at which the vapor pressure of the solid and liquid phases are equal. The freezing point at standard pressure corresponds to point C.

Q-20 If a nonvolatile solute is dissolved in a pure liquid, it is observed that the vapor pressure is lowered.

On the graph below, the effect of vapor pressure lowering on the line CD has been indicated by a dotted line FG. Complete the figure by showing the effect of vapor pressure lowering on the line AD.

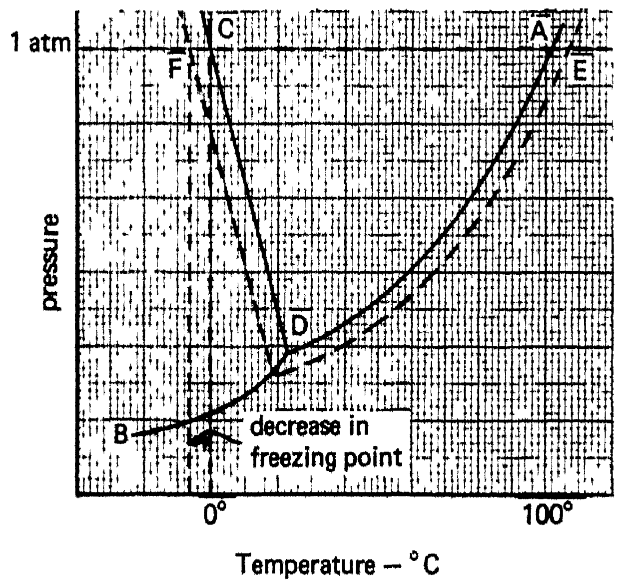


A-20



Q-21 How has the vapor pressure lowering affected the freezing point of the solution?

A-21 The freezing point has been lowered to point F.



S-3 The freezing point depression is a <u>colligative property</u>, i. e., it is a property which depends only on the number of solute particles in solution and not on the nature of the solute particles. If one mole of solute particles is dissolved in 1000 g of pure solvent, the change in freezing point is always the same and is <u>characteristic of the solvent.</u>

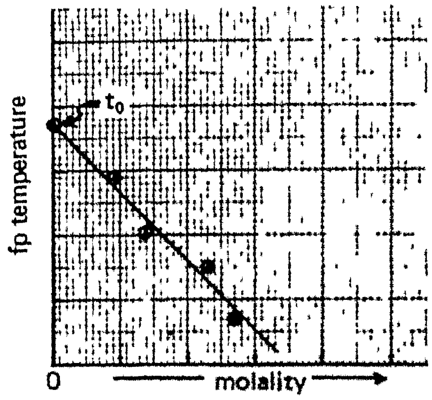
Q-22 If one mole of nonvolatile particles is dissolved in 1000 g of water, the freezing point is 1.86°C lower than that of pure water. The <u>molal freezing point depression constant</u>, K_f, for water is, thus, 1.86 deg/molal.

A mole of a sugar is dissolved in 1000 g of water. What is the freezing point of the solution?

A-22 $T_f = 0.00°C - 1\ 86°C$

$= -1.86°C$

Q-23 Below is a plot of freezing point vs the molal concentration for a series of dilute solutions.



The slope of the line is equal to $-K_f$, where K_f is defined as the molal freezing point depression constant. The point t_0 is the freezing point of the pure solvent.

a) Derive an equation which relates the freezing point of a solution, t, molality, m, the constant K_f, and the freezing point of the pure solvent, t_0.

b) Derive an equation for the freezing point depression ($t_0 - t = \Delta T$).

A-23 The equation of a straight line has the form:

$$y = ax + b$$

In the plot, $y = t$, $a = -K_f$, $x = m$, and $b = t_0$.

Therefore

$$t = -K_f m + t_0$$
$$t_0 - t = \Delta T = K_f m$$

Q-24 What is the freezing point of a 2.00 molal solution of a sugar in water?

A-24 $\Delta T = K_f m$

$$= \begin{array}{c|c} 1.86°\text{C} & 2.00\ \cancel{\text{molal}} \\ \hline \cancel{\text{molal}} & \end{array}$$

$= 3\ 72°C$

$T_f = 0.00°C - 3.72°C$

$= -3.72°C$

Q-25 Calculate the freezing point of a solution which has 0.100 mole of a sugar dissolved in 250 g of water.

A-25 $$\begin{array}{c|c} 0.100\ \text{mole} & 1000\ \cancel{\text{g}} \\ \hline 250\ \cancel{\text{g}} & 1\ \text{kg} \end{array}$$

$= 0.400$ mole/kg $= 0.400$ molal

$\Delta T = K_f m$

$$= \begin{array}{c|c} 1.86°\text{C} & 0.400\ \cancel{\text{molal}} \\ \hline \cancel{\text{molal}} & \end{array}$$

$= 0.744°C$

$T_f = 0.000 - 0.744°C = -0.744°C$

Q-26 Calculate the freezing point of a solution made by dissolving 34.2 g of a sugar in 500 g of water. The molecular weight of the sugar is 342.

A-26
$$\frac{34\ 2\ \cancel{\text{g sugar}}}{500\ \cancel{\text{g } H_2O}}\ \Bigg|\ \frac{1\text{ mole sugar}}{342\ \cancel{\text{g sugar}}}\ \Bigg|\ \frac{1000\ \cancel{\text{g } H_2O}}{1\text{ kg } H_2O}$$
$$= 0\ 200\ \frac{\text{mole sugar}}{1\text{ kg } H_2O} = 0\ 200\text{ molal}$$
$$\Delta T = K_f m$$
$$= \frac{1\ 86°C}{\cancel{\text{molal}}}\ \Bigg|\ \frac{0\ 200\ \cancel{\text{molal}}}{}$$
$$= 0\ 372°C$$
$$T_f = 0\ 000 - 0\ 372°C = -0\ 372°C$$

Q-27 Calculate the freezıng poınt of a solutıon made by dıssolvıng 42 0 g of mannoheptose, $C_7H_{14}O_7$, ın 100 g of water

(Assume that the solute ıs nonvolatıle)

A-27
$$\frac{42\ 0\ \cancel{\text{g } C_7H_{14}O_7}}{100\ \cancel{\text{g } H_2O}}\ \Bigg|\ \frac{1\text{ mole } C_7H_{14}O_7}{210\ \cancel{\text{g } C_7H_{14}O_7}}\ \Bigg|\ \frac{1000\ \cancel{\text{g } H_2O}}{1\text{ kg } H_2O}$$
$$= 2\ 00\ \frac{\text{mole } C_7H_{14}O_7}{1\text{ kg } H_2O} = 2\ 00\text{ molal}$$
$$\Delta T = K_f m$$
$$= \frac{1\ 86°C}{\cancel{\text{molal}}}\ \Bigg|\ \frac{2\ 00\ \cancel{\text{molal}}}{}$$
$$= 3.72°C$$
$$T_f = 0\ 00°C - 3.72°C = -3.72°C$$

Q-28 The freezıng poınt depressıon constant for camphor ıs 37.7°C/molal. The normal freezıng poınt ıs 178.4°C Calculate the freezıng poınt of solutıon made by dıssolving 20.0 g of an organıc solute, Y, wıth a MW of 150, ın 100 g of camphor.

(Assume that the solute is nonvolatile)

A-28
$$\frac{20\ 0\ \cancel{\text{g Y}}}{100\ \cancel{\text{g camphor}}}\ \Bigg|\ \frac{1\text{ mole Y}}{150\ \cancel{\text{g Y}}}\ \Bigg|\ \frac{1000\ \cancel{\text{g camphor}}}{1\text{ kg camphor}}$$
$$= \frac{1.33\text{ mole Y}}{1\text{ kg camphor}} = 1\ 33\text{ molal}$$
$$\Delta T = K_f m = \frac{37.7°C}{\cancel{\text{molal}}}\ \Bigg|\ \frac{1\ 33\ \cancel{\text{molal}}}{}$$
$$= 50\ 1°C$$
$$T_f = 178\ 4°C - 50\ 1°C = 128\ 3°C$$

Q-29 The freezing point depression constant K_f (often called the cryoscopic constant) for benzene, C_6H_6, is 5.12°C/molal. The normal freezing point of benzene is 5.48°C.
Calculate the freezing point of a solution made by dissolving 30.0 g of an organic solute, X, with a MW of 175, in 50.0 g of benzene.

(Assume that the solute is nonvolatile.)

A-29
$$\frac{30.0\ \cancel{\text{g X}}}{50\ 0\ \cancel{\text{g } C_6H_6}}\ \Bigg|\ \frac{1\text{ mole X}}{175\ \cancel{\text{g X}}}\ \Bigg|\ \frac{1000\ \cancel{\text{g } C_6H_6}}{1\text{ kg } C_6H_6}$$
$$= 3\ 43\ \frac{\text{mole X}}{1\text{ kg } C_6H_6} = 3.43\text{ molal}$$
$$\Delta T = K_f m = \frac{5.12°C}{\cancel{\text{molal}}}\ \Bigg|\ \frac{3.43\ \cancel{\text{molal}}}{}$$
$$= 17.6°C$$
$$T_f = 5\ 48°C - 17.6°C = -12.1°C$$

Q-30 Calculate the value of K_f for urethane given the following data.
Freezing point of pure urethane = 49.7°C.
A solution made by dissolving 10.0 g of a nonvolatile organic solute, Z, in 30.0 g of urethane freezes at 36.5°C.
MW of Z = 130.

A-30 $\Delta T = K_f m$

$K_f = \frac{\Delta T}{m}$

$\Delta T = 49\ 7°C - 36\ 5°C = 13\ 2°C$

$m = \frac{10\ 0\ \cancel{g\ Z}}{30.0\ \cancel{g\ urethane}} \left| \frac{1000\ \cancel{g\ urethane}}{1\ kg\ urethane} \right| \frac{1\ mole\ Z}{130\ \cancel{g\ Z}}$

$= \frac{2.56\ mole\ Z}{1\ kg\ urethane} = 2.56\ molal$

$K_f = \frac{13\ 2°C}{2\ 56\ molal} = 5.16°C/molal$

Q-31 Freezing point depression data may be used to calculate the molecular weight of an unknown substance. The molecular formula may also be calculated if the empirical formula is known from analytical data.
A solution made by dissolving 90.0 g of glucose in 1000 g of water freezes at -0 93°C. Calculate the molality of this solution

(Assume that the solute is nonvolatile.)

A-31 $\Delta T = K_f m$

$m = \frac{0\ 93\cancel{°C}}{} \left| \frac{1\ molal}{1.86\cancel{°C}} \right.$

$= 0.50\ molal = 0\ 50 \frac{mole\ glucose}{1\ kg\ H_2O}$

Q-32 If 90.0 g of glucose is equivalent to 0.50 mole of glucose, what is the weight of one mole of glucose?

A-32 $\frac{90\ 0\ g}{0.50\ mole} = 180\ g/mole$

Q-33 Analytical data show that the empirical formula for glucose is CH_2O. What is the molecular formula?

A-33 The molecular formula is some multiple of CH_2O, which may be represented by $(CH_2O)_n$.

The empirical formula weight is

$12.0 + 2(1.00) + 16.0 = 30.0$

$n = \frac{180}{30} = 6$

The molecular formula is

$(CH_2O)_6 = C_6H_{12}O_6$.

Q-34 A solution made by dissolving 45.0 g of arabinose in 500 g of water freezes at -1.13°C.
Calculate the molecular weight of arabinose.

(Hint: Calculate molality first.)

(Assume that the solute is nonvolatile.)

A-34 $\Delta T = K_f m$

$m = \frac{1.13\cancel{°C}}{} \left| \frac{1\ molal}{1.86\cancel{°C}} \right.$

$= 0.608\ molal = 0\ 608 \frac{mole}{1\ kg}$

90.0 g arabinose = 0.608 mole

$\frac{90.0}{0.608}\ g/mole = 148\ g/mole$

Q-35 The empirical formula of arabinose is CH_2O.
Calculate the molecular formula of arabinose.

A-35 The empirical formula weight is

$12.0 + 2(1.00) + 16.0 = 30.0$

The molecular formula is given by $(CH_2O)_n$

$n = \frac{148}{30.0} \approx 5$

The molecular formula is

$(CH_2O)_5 = C_5H_{10}O_5$

The data show that molecular weights determined by freezing point depression are not exact. The exact molecular weight of arabinose is 150. (3 significant figures.)

Q-36 A solution made by dissolving 4.00 g of an organic solute, A, in 50.0 g of benzene freezes at 3.74°C.

K_f for benzene = 5.12°C/molal
Freezing point of pure benzene = 5.48°C

Calculate the molecular weight and molecular formula of A. The empirical formula of A is C_3H_2Br.

(Assume that the solute is nonvolatile.)

A-36 $\Delta T = K_f m$

$\Delta T = 5.48°C - 3.74°C = 1.74°C$

$$m = \frac{1.74\cancel{°C}}{} \left| \frac{1 \text{ molal}}{5.12\cancel{°C}} \right. = 0.340 \text{ molal}$$

$$= 0.340 \frac{\text{mole A}}{1 \text{ kg } C_6H_6}$$

$$\frac{4.00 \text{ g A}}{50.0 \cancel{\text{g } C_6H_6}} \left| \frac{1000 \cancel{\text{g } C_6H_6}}{1 \cancel{\text{kg } C_6H_6}} \right| \frac{1 \cancel{\text{kg } C_6H_6}}{0.340 \text{ mole A}}$$

$= 235$ g A/mole A

The molecular formula is given by $(C_3H_2Br)_n$.

The empirical formula weight is

$3(12.0) + 2(1.00) + 79.9 = 118$

$n = \frac{235}{118} \approx 2$

The molecular formula is

$(C_3H_2Br)_2 = C_6H_4Br_2$.

$\Delta T = K_f m$

ΔT = change in freezing point

K_f = freezing point depression or cryoscopic constant

m = molality

S-4 If a solute, AB, dissociates in solution, the dissociation may be represented by the following equation.

$$AB \rightleftharpoons A^+ + B^-$$

If the reaction proceeds to completion, AB is said to be 100% dissociated, i.e., 100% of the AB molecules have dissociated, and the only particles in solution are A^+ and B^-. If AB is less than 100% dissociated in solution, three kinds of particles exist in solution, AB, A^+ and B^-. If a 1.00 molal solution of AB were 50% dissociated, then

$$\text{molality of AB} = 1.00 - (0.50)(1.00) = 0.50$$

$$\text{molality of } A^+ = \text{molality of } B^- = 0.50$$

$$\text{Total molality of particles in solution} = \text{molality of AB} + \text{molality of } A^+ + \text{molality of } B^- = 0.50 + 0.50 + 0.50 = 1.50$$

Q-37 If a substance dissociates in solution, the number of particles in solution is greater than the number of molecules placed in solution The dissociated particles lower the vapor pressure just as undissociated particles do

What is the freezing point of a 1 00 molal NaCl solution if NaCl is assumed to be 100% dissociated?

(Hint Calculate the molal concentration of all particles in the solution)

A-37 Each NaCl that dissociates gives 2 ions (Na^+ and Cl^-) Therefore, the concentration of particles is 2 00 molal, and the freezing point depression is

$\Delta T = m(K_f)$

$= 2\ 00\ (1\ 86) = 3\ 72$

$T_f = -3\ 72°C$

Q-38 A substance CD is 4 00% dissociated in aqueous solution What is the freezing point of a 0 100 molal aqueous solution of CD

(Assume that the solute is nonvolatile.)

A-38 If a 0 100 molal solution of CD is 4.00% dissociated, then

molality of CD = 0 100 - (0 0400)(0 100)

= 0 100 - 0.004 = 0 096

molality of C = molality of D = 0 004

Total concentration of particles in solution is

0 096 + 0 004 + 0 004 = 0 104

$\Delta T = K_f m$

$= (1\ 86\ \text{deg}/\cancel{\text{molal}})(0\ 104\ \cancel{\text{molal}})$

$= 0\ 193\ \text{deg}$

$T_f = -0\ 193°C$

Q-39 KBr is 79 0% dissociated in solution What is the freezing point of a 0.500 molal aqueous solution?

A-39 If a 0 500 molal solution of KBr is 79.0% dissociated, then

molality of KBr = 0 500 - (0 790)(0 500)

= 0 500 - 0 395 = 0 105

molality of K^+ = molality of Br^- = 0 395

The total concentration of particles is

0 105 + 0 395 + 0 395 = 0 895

$\Delta T = K_f m$

$= (1\ 86\ \text{deg}/\cancel{\text{molal}})(0\ 895\ \cancel{\text{molal}})$

$= 1\ 66\ \text{deg}$

$T_f = -1\ 66°C$

Q-40 A 0 100 molal aqueous solution of a partially dissociated substance, AB, freezes at -0 208°C Calculate the percent dissociation

(Hint Let x = total concentration of particles in solution and y = molality of A = molality of B)

(Assume that the solute is nonvolatile)

A-40 If no dissociation occurred in a 0.100 molal solution, the freezing point depression would be

$$\Delta T = (1.86\ \text{deg}/\cancel{\text{molal}})(0.100\ \cancel{\text{molal}})$$
$$= 0.186\ \text{deg}$$

Let x = total concentration of particles, then

$$\Delta T = (x)(1.86) = 0.208$$

$$x = \frac{0.208}{1.86} = 0.112$$

If AB dissociates as follows

$$AB \rightleftarrows A^+ + B^-$$
$$(0.100 - y)\quad (y)\quad (y)$$

The total concentration of particles is

$$(0.100 - y) + y + y = 0.112$$
$$y + 0.100 = 0.112$$
$$y = 0.012$$
$$= \text{molality of } A^+ \text{ and } B^-$$
$$= \text{molality of AB molecules dissociated}$$

$$\%\ \text{dissociation} = \frac{0.012}{0.100}(100) = 12\%$$

Q-41 A 0.100 molal solution of acetic acid in water freezes at -0.190°C. Calculate the percent dissociation of acetic acid at this temperature.

A-41 If x = total concentration of particles, then

$$\Delta T = (x)(1.86) = 0.190$$

$$x = \frac{0.190}{1.86} = 0.102$$

If acetic acid dissociates according to the equation

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$
$$(0.100 - y)\quad (y)\quad (y)$$

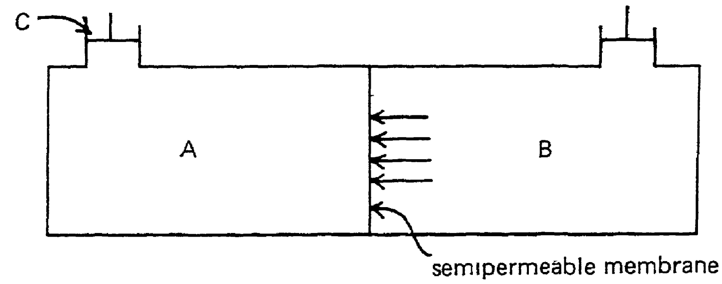
The total concentration of particles is

$$(0.100 - y) + y + y = 0.102$$
$$y + 0.100 = 0.102$$
$$y = 0.002$$
$$= \text{molality of } CH_3COO^- \text{ and } H^+$$
$$= \text{molality of } CH_3COOH \text{ molecules dissociated}$$

$$\%\ \text{dissociation} = \frac{0.002}{0.100}(100) = 2\%$$

[redacted]

S-5 The diagram below shows two aqueous solutions of different vapor pressures separated by a semipermeable membrane that permits the passage of water molecules but prevents the passage of solute molecules If the vapor pressure of solution A is lower than that of solution B, water molecules will pass from chamber B to chamber A to decrease the difference in vapor pressure The passage of the water through the membrane is called osmosis



	Q-42 In the figure in S-5, what happens to the volume of the solution in chamber A as the water passes through the membrane?
A-42 The volume increases	Q-43 What happens to the piston, C?
A-43 The piston is pushed upward	Q-44 How could the upward displacement of the piston be prevented?
A-44 The upward displacement could be prevented by applying pressure to the piston.	R When two solutions of unequal vapor pressure are separated by a semipermeable membrane, solvent molecules will pass from the solution of higher vapor pressure into the solution of lower vapor pressure (osmosis).

S-6 The mechanical pressure which must be applied to a solution in chamber A to prevent osmosis when pure solvent is in chamber B is called <u>osmotic pressure</u> The osmotic pressure of a solution is directly proportional to the concentration of solute and the temperature of the solution, i e ,

$$\pi \text{ (osmotic p)} = \text{(constant)(concentration)(Temperature)}$$
$$= aCT$$

If C is in moles/liter then

$$\pi = a\left(\frac{n}{V}\right) T$$

or

$$\pi V = naT$$

Note the similarity to the gas law equation PV = nRT.

	Q-45 Calculate the value of the constant, a, from the following data π = 2 95 atm V = 1 00 liter $n = \frac{45\ 1\ g}{342\ g/mole}$ T = 273°K

A-45 $\pi V = naT$

$$a = \frac{\pi V}{nT}$$

$$= \frac{(2.95 \text{ atm})(1.00 \text{ liter})}{\left(\frac{45.1 \text{ g}}{342 \text{ g/mole}}\right)(273°)}$$

$$= \frac{(2.95)(342)}{(45.1)(273)} \frac{\text{liter-atm}}{\text{deg-mole}}$$

$$= 0.0819 \frac{\text{liter-atm}}{\text{deg-mole}}$$

This agrees closely with the gas law constant

Therefore, $\pi V = nRT$

Q-46 75.0 g of glucose, $C_6H_{12}O_6$, is present in 250 ml of aqueous solution at 300°K. What is the osmotic pressure of the solution?

A-46 $MW_{C_6H_{12}O_6} = 6(12.0) + 12(1.00) + 6(16.0)$
$= 180$

$$n = \frac{75.0 \cancel{\text{g}}}{} \Big| \frac{1 \text{ mole}}{180 \cancel{\text{g}}}$$

$= 0.417$ mole

$$\pi = R\left(\frac{n}{V}\right)T$$

$$= \frac{0.082 \cancel{\text{liter}}\text{-atm}}{\cancel{\text{deg-mole}}} \Big| \frac{0.417 \cancel{\text{mole}}}{0.250 \cancel{\text{liter}}} \Big| \frac{300 \cancel{\text{deg}}}{}$$

$= 41$ atm

Q-47 An aqueous solution of glucose, $C_6H_{12}O_6$, has an osmotic pressure of 2.72 atm at 298°K. How many moles of glucose were dissolved per liter of solution?

A-47 $\pi = RCT$

$$C = \frac{\pi}{RT}$$

$$= \frac{(2.72 \cancel{\text{atm}})}{\left(0.082 \frac{\text{liter-}\cancel{\text{atm}}}{\cancel{\text{deg}}\text{-mole}}\right)(298 \cancel{\text{deg}})}$$

$$= \left(\frac{2.72}{24}\right) \text{mole/liter}$$

$= 0.11$ mole/liter

Q-48 How many grams of glucose were dissolved per liter of solution in the solution given in Q-47?

A-48 0.11 moles/liter dissolved

180 g/mole = MW glucose

Therefore, the number of grams of glucose that dissolved is

$$\frac{0.11 \cancel{\text{mole}}}{\text{liter}} \Big| \frac{180 \text{ g}}{\cancel{\text{mole}}}$$

$= 20$ g/liter

Q-49 Calculate the molecular weight of the solute in the following solution.

10.0 g of solute are dissolved in enough water to make a liter of solution. The osmotic pressure of the resulting is 1.18 atm at 273°K.

(Hint: $C = \frac{n}{V} = \frac{g/MW}{V}$)

A-49 $\pi = RCT$

$$= R(n/V)T$$

$$= R\left(\frac{g/MW}{V}\right)T$$

$$MW = \frac{gRT}{\pi V}$$

$$= \frac{(10.0\,g)(0.082\ \cancel{liter}\text{-}\cancel{atm}/\cancel{deg}\text{-mole})(273\ \cancel{deg})}{(1.18\ \cancel{atm})(1.00\ \cancel{liter})}$$

$$= 190\ g/mole$$

R $\pi V = nRT$

π = osmotic pressure

V = volume of solution

n = moles of solute

R = constant $\left(0.082\ \frac{\text{liter-atm}}{\text{deg-mole}}\right)$

T = absolute temperature

NOTES

Chapter 7 THERMODYNAMICS AND KINETICS

Part I Why Reactions Occur

After completing this section you should be able to

a) compute the transfer of energy that accompanies any chemical reaction
b) show the relationship between thermodynamic quantities and how they relate to chemical changes
c) predict if a chemical reaction will occur

Part II Rates of Reactions

After completing this section you should be able to

a) determine rate expressions from experimental data
b) compute rates and rate constants for chemical reactions
c) propose a path by which reactants could be converted into products

Part III· Introduction to Equilibrium

After completing this section you should be able to

a) determine the extent to which reactants are converted to products
b) express the relationship between thermodynamic quantities and the extent to which a reaction occurs
c) evaluate thermodynamic quantities from experimentally determined equilibrium constants.

PART I: Why Reactions Occur

S-1 Heat is that form of energy which passes from one body to another as the result of a temperature difference between the two bodies The amount of energy transferred is expressed in the unit of calories One calorie is the amount of heat needed to raise the temperature of one gram of H_2O one degree centigrade

Q-1 Why does a block of ice feel cold to your touch?

A-1 When your finger touches the block of ice which is at a lower temperature, heat is transferred from your finger to the block of ice The loss in heat from your finger makes the block of ice feel cold

Q-2 According to the kinetic molecular theory, in order to boil a substance the molecules must obtain enough energy to overcome the forces of attraction between neighboring molecules. Describe how this energy is obtained when a substance such as water is boiled over a campfire.

A-2 A flame is placed under a container of water and energy is transferred from the hot flame to the cool water. This heat increases the kinetic energy of the water molecules

Q-3 One calorie (cal) is the amount of heat needed to raise the temperature of 1 gram of H_2O 1°C. A quantity of 10 grams of water at 10°C has 60 calories of heat transferred to it. What is the final temperature of the water?

A-3 increase in temp $= \dfrac{60\,\cancel{\text{cal}}}{} \bigg| \dfrac{1\,\cancel{\text{g H}_2\text{O}}\ ^\circ\text{C}}{1\,\cancel{\text{cal}}} \bigg| \dfrac{}{10\,\cancel{\text{g H}_2\text{O}}}$

$= 10°C + 6°C = 16°C$

Q-4 How much heat (in calories) is necessary to raise the temperature of 25 grams of H_2O 25°C?

A-4 $\dfrac{25\,\cancel{\text{g H}_2\text{O}}}{} \bigg| \dfrac{1\text{ cal}}{1\,\cancel{\text{g H}_2\text{O}};\ \cancel{^\circ\text{C}}} \bigg| \dfrac{25\,\cancel{^\circ\text{C}}}{} = 620\text{ cal}$

Q-5 Specific heat is the heat necessary to raise one gram of a substance one degree centigrade (cal/g-degrees) What is the value for the specific heat of water?

A-5 1.00 cal/deg-g

Q-6 If the specific heat of a substance is 0.876 cal/deg-g, how much heat is necessary to raise 500 gm of the material from a temperature of 20.0°C to a temperature of 80.0°C? Express in kilocalories.
1 kilocalorie (kcal) = 1000 calories

A-6 Change in temp. = 80.0 - 20.0 = 60.0°C

$\dfrac{500\,\cancel{\text{g}}}{} \bigg| \dfrac{0.876\,\cancel{\text{cal}}}{\cancel{\text{g}} - \cancel{\text{deg}}} \bigg| \dfrac{60.0^\circ}{} \bigg| \dfrac{1\text{ kcal}}{1000\,\cancel{\text{cal}}} =$

26.3 kcal

Q-7 What will be the final temperature of 1000 g of material at 25.0°C after 7.00 kcal of heat is transferred away from it? The specific heat of the material is 1.10 cal/deg-g

A-7 loss in temp $= \dfrac{7\ 00\ \cancel{kcal}}{} \Big| \dfrac{1000\ \cancel{cal}}{1\ \cancel{kcal}} \Big| \dfrac{deg\text{-}\cancel{g}}{1\ 10\ \cancel{cal}} \Big| \dfrac{}{1000\ \cancel{g}} = 6\ 4°C$

25 0°C - 6 4°C = 18 6°C

R a) 1 cal = heat needed to raise the temperature of 1 g of H_2O 1°C

b) specific heat = amount of heat necessary to raise one gram of material one degree centigrade, cal/deg-g.

S-2 In a chemical reaction, heat is absorbed or released For example· one mole of A can react with one mole of B to form one mole of C and give off 60 kcal of heat This can be written in equation form as A + B → C + 60 kcal This heat absorbed or released in a chemical reaction is called the enthalpy change for the reaction, ΔH The Δ refers to the difference in the sum of the enthalpies of the reactants and the products The enthalpy change is expressed mathematically as $\Delta H = \sum_i n_i H_i$ (products) - $\sum_i n_i H_i$ (reactants) where H_i and n_i are the enthalpy and moles, respectively, of the i^{th} substance

Q-8 What is the enthalpy change (ΔH) for the chemical reaction A → B if H for compound A is 50 kcal/mole and H for compound B is 100 kcal/mole

A-8 Conversion of one mole of A into one mole of B

$\Delta H = \Sigma nH$ (products) - ΣnH (reactants)

ΔH = (1 mole)(100 kcal/mole) - (1 mole)(50 kcal/mole)

= 50 kcal

Q-9 The enthalpy of a substance can be considered as a measure of the amount of energy the substance contains This is often referred to as heat content Two substances A and B have heat contents of 100 and 150, respectively. Which substance has the greater energy? Why?

A-9 B Since H is a measure of the heat content, the substance with the larger heat content will have the greater energy.

Q-10 If in a chemical reaction, A → B, heat is given off, is the enthalpy of the product greater or less than that of the reactants? Why?

A-10 The enthalpy of the product must be lower because energy is released in going from the reactant to the product.

Q-11 A chemical reaction which gives off heat is called an exothermic reaction. What is the sign of ΔH for this type of reaction? Why?

A-11 Negative Since heat is given off in the reaction, the sum of the enthalpies of the products must be less than the sum of the enthalpies of the reactants.

$$\Delta H = \Sigma nH_{(products)} - \Sigma nH_{(reactants)}$$

in order for ΔH to be negative

$$\Sigma nH_{(reactants)} > \Sigma nH_{(products)}$$

Q-12 A chemical reaction which absorbs heat is called an endothermic reaction. Is the energy of the products greater or less than that of the reactants? Why?

A-12 Greater If heat is absorbed in the reaction, ΔH for the reaction is positive Since

$$\Delta H = \Sigma nH_{(products)} - \Sigma nH_{(reactants)}$$

in order for ΔH to be positive

$$\Sigma nH_{(products)} > \Sigma nH_{(reactants)}$$

Q-13 If the enthalpies of products and reactants are given in kilocalories/mole for the reaction $A + B \rightarrow C$, the enthalpy change, ΔH, for the conversion of one mole of A and one mole of B into one mole of C is -30 kcal What is ΔH for the reaction if 2 moles of C are formed?

A-13 If 2 moles of C are formed, the reaction would be $2A + 2B \rightarrow 2C$

ΔH = -30 kcal/mole of C formed

For two moles,

ΔH = (2 moles)(-30 kcal/mole)

= -60 kcal

Q-14 What is the enthalpy change for the reaction

$$CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca(OH)_{2(s)}$$

if $H_{CaO_{(s)}}$ = -151.8 kcal/mole

$H_{H_2O_{(\ell)}}$ = -68.4 kcal/mole

$H_{Ca(OH)_{2(s)}}$ = -235.4 kcal/mole ?

A-14 For the conversion of one mole of CaO and one mole of H_2O into one mole of $Ca(OH)_2$,

$$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$$

ΔH = [(1 mole)(-235 4 kcal/mole)] - [(1 mole)(-68 4 kcal/mole) + (1 mole)(-151.8 kcal/mole)]

ΔH = -15 2 kcal.

Q-15 Is the reaction given in Q-14, exothermic or endothermic?

A-15 ΔH = negative value. Therefore, the reaction is exothermic (gives off energy)

Q-16 What is the enthalpy change for the reaction

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

if H_{CO} = -26.4 kcal/mole

H_{O_2} = 0.0

H_{CO_2} = -94.0 kcal/mole?

Is the reaction endothermic or exothermic?

A-16 For the conversion of one mole of CO and one half mole of O_2 into one mole of CO_2,

$$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$$

ΔH = [(1 mole)(-94.0 kcal/mole)] - [(0.0) + (1 mole)(-26.4 kcal/mole)]

ΔH = -67.6 kcal.

The reaction is exothermic.

Q-17 What is the enthalpy change for the reaction

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} ?$$

(See Q-16 for enthalpies.)

A-17 For the conversion of two moles of CO and one mole of O_2 into two moles of CO_2,

$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(2 \text{ moles})(-94\ 0 \text{ kcal/mole})] - [0\ 0 + (2 \text{ moles})(-26\ 4 \text{ kcal/mole})]$

$\Delta H = -135\ 2 \text{ kcal}$

Q-18 What is the enthalpy change for the reaction

$$CH_{4(g)} + C_2H_{4(g)} \rightarrow C_3H_{8(g)}$$

if $H_{CH_{4(g)}} = -17\ 9$ kcal/mole

$H_{C_2H_{4(g)}} = 12\ 5$ kcal/mole

$H_{C_3H_{8(g)}} = -24\ 8$ kcal/mole ?

Is the reaction exothermic or endothermic?

A-18 For the conversion of one mole of CH_4 and one mole of C_2H_4 into one mole of C_3H_8,

$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(1 \text{ mole})(-24.8 \text{ kcal/mole})] - [(1 \text{ mole})(12\ 5 \text{ kcal/mole}) + (1 \text{ mole})(-17\ 9 \text{ kcal/mole})]$

$\Delta H = -19\ 4$ kcal.

The reaction is exothermic.

Q-19 What is the enthalpy change for the reaction $C_3H_{8(g)} \rightarrow C_2H_{4(g)} + CH_{4(g)}$?

Is the reaction exothermic or endothermic?

A-19 For the conversion of one mole of C_3H_8 into one mole of C_2H_4 and one mole of CH_4,

$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(1 \text{ mole})(12.5 \text{ kcal/mole}) + (1 \text{ mole})(-17.9 \text{ kcal/mole})] - [(1 \text{ mole})(-24.8 \text{ kcal/mole})]$

$\Delta H = +19.4$ kcal.

Notice that $\Delta H_{(forward)} = -\Delta H_{(reverse)}$ for any chemical reaction.

The reaction is endothermic.

Q-20 What is the enthalpy change for the reaction $C_2H_6O_{2(g)} \rightarrow 2H_2O_{(\ell)} + C_2H_{2(g)}$

if $H_{C_2H_6O_{2(g)}} = -126.3$ kcal/mole

$H_{H_2O_{(\ell)}} = -68.3$ kcal/mole

$H_{C_2H_{2(g)}} = 54.2$ kcal/mole ?

Is the reaction exothermic or endothermic?

A-12 Greater If heat is absorbed in the reaction, ΔH for the reaction is positive. Since

$$\Delta H = \Sigma nH_{(products)} - \Sigma nH_{(reactants)}$$

in order for ΔH to be positive

$$\Sigma nH_{(products)} > \Sigma nH_{(reactants)}$$

Q-13 If the enthalpies of products and reactants are given in kilocalories/mole for the reaction $A + B \rightarrow C$, the enthalpy change, ΔH, for the conversion of one mole of A and one mole of B into one mole of C is -30 kcal What is ΔH for the reaction if 2 moles of C are formed?

A-13 If 2 moles of C are formed, the reaction would be $2A + 2B \rightarrow 2C$

ΔH = -30 kcal/mole of C formed

For two moles,

ΔH = (2 moles)(-30 kcal/mole)

= -60 kcal

Q-14 What is the enthalpy change for the reaction

$$CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca(OH)_{2(s)}$$

if $H_{CaO_{(s)}}$ = -151 8 kcal/mole

$H_{H_2O_{(\ell)}}$ = -68 4 kcal/mole

$H_{Ca(OH)_{2(s)}}$ = -235 4 kcal/mole ?

A-14 For the conversion of one mole of CaO and one mole of H_2O into one mole of $Ca(OH)_2$,

$$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$$

ΔH = [(1 mole)(-235 4 kcal/mole)] - [(1 mole)(-68 4 kcal/mole) + (1 mole)(-151 8 kcal/mole)]

ΔH = -15 2 kcal

Q-15 Is the reaction given in Q-14, exothermic or endothermic?

A-15 ΔH = negative value Therefore, the reaction is exothermic (gives off energy)

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$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

if H_{CO} = -26.4 kcal/mole

H_{O_2} = 0.0

H_{CO_2} = -94.0 kcal/mole?

Is the reaction endothermic or exothermic?

A-16 For the conversion of one mole of CO and one half mole of O_2 into one mole of CO_2,

$$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$$

ΔH = [(1 mole)(-94 0 kcal/mole)] - [(0.0) + (1 mole)(-26.4 kcal/mole)]

ΔH = -67 6 kcal

The reaction is exothermic.

Q-17 What is the enthalpy change for the reaction

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \ ?$$

(See Q-16 for enthalpies.)

A-17 For the conversion of two moles of CO and one mole of O_2 into two moles of CO_2,

$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(2 \text{ moles})(-94\ 0 \text{ kcal/mole})] - [0\ 0 + (2 \text{ moles})(-26\ 4 \text{ kcal/mole})]$

$\Delta H = -135\ 2 \text{ kcal}$

Q-18 What is the enthalpy change for the reaction

$$CH_{4(g)} + C_2H_{4(g)} \rightarrow C_3H_{8(g)}$$

if $H_{CH_{4(g)}} = -17\ 9$ kcal/mole

$H_{C_2H_{4(g)}} = 12\ 5$ kcal/mole

$H_{C_3H_{8(g)}} = -24\ 8$ kcal/mole ?

Is the reaction exothermic or endothermic?

A-18 For the conversion of one mole of CH_4 and one mole of C_2H_4 into one mole of C_3H_8,

$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(1 \text{ mole})(-24\ 8 \text{ kcal/mole})] - [(1 \text{ mole})(12\ 5 \text{ kcal/mole}) + (1 \text{ mole})(-17\ 9 \text{ kcal/mole})]$

$\Delta H = -19\ 4 \text{ kcal}$

The reaction is exothermic

Q-19 What is the enthalpy change for the reaction $C_3H_{8(g)} \rightarrow C_2H_{4(g)} + CH_{4(g)}$?

Is the reaction exothermic or endothermic?

A-19 For the conversion of one mole of C_3H_8 into one mole of C_2H_4 and one mole of CH_4,

$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(1 \text{ mole})(12\ 5 \text{ kcal/mole}) + (1 \text{ mole})(-17\ 9 \text{ kcal/mole})] - [(1 \text{ mole})(-24.8 \text{ kcal/mole})]$

$\Delta H = +19\ 4 \text{ kcal}$

Notice that $\Delta H_{(forward)} = -\Delta H_{(reverse)}$ for any chemical reaction

The reaction is endothermic

Q-20 What is the enthalpy change for the reaction $C_2H_6O_{2(g)} \rightarrow 2H_2O_{(\ell)} + C_2H_{2(g)}$

if $H_{C_2H_6O_{2(g)}} = -126\ 3$ kcal/mole

$H_{H_2O_{(\ell)}} = -68.3$ kcal/mole

$H_{C_2H_{2(g)}} = 54.2$ kcal/mole ?

Is the reaction exothermic or endothermic?

A-20 For the conversion of one mole of $C_2H_6O_2$ into two moles of H_2O and one mole of C_2H_2,

$$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$$

$$\Delta H = [(2 \text{ moles})(-68.3 \text{ kcal/mole}) + (1 \text{ mole})(54.2 \text{ kcal/mole})] - [(1 \text{ mole})(-126.3 \text{ kcal/mole})]$$

$$\Delta H = 43.9 \text{ kcal}$$

The reaction is endothermic

Q-21 What is the enthalpy change for the reaction

$$2H_2O_{(g)} + C_2H_{2(g)} \rightarrow C_2H_6O_{2(g)} \; ?$$

Is the reaction endothermic or exothermic?

A-21 $\Delta H_{(forward)} = -\Delta H_{(reverse)}$

Therefore, $\Delta H = -43.9$ kcal, and the reaction is exothermic

Q-22 What is the enthalpy of $C_2H_6O_{(g)}$ if the enthalpy change for the reaction

$$C_2H_{4(g)} + H_2O_{(g)} \rightarrow C_2H_6O_{(\ell)}$$

is -21.0 kcal and

$$H_{C_2H_{4(g)}} = 12.5 \text{ kcal/mole}$$

$$H_{H_2O_{(g)}} = -57.8 \text{ kcal/mole} \; ?$$

A-22 $\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$$-21.0 \text{ kcal} = [(1 \text{ mole})(H_{C_2H_6O})] - [(1 \text{ mole})(12.5 \text{ kcal/mole}) + (1 \text{ mole})(-57.8 \text{ kcal/mole})]$$

$$H_{C_2H_6O_{(\ell)}} = \frac{-21.0 \text{ kcal} + 12.5 \text{ kcal} - 57.8 \text{ kcal}}{1 \text{ mole}}$$

$$= -66.3 \text{ kcal/mole}$$

Q-23 What is the enthalpy of $CaCO_{3(s)}$ if the enthalpy change for the reaction

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

is 42.6 kcal and

$$H_{CO_{2(g)}} = -94.0 \text{ kcal/mole}$$

$$H_{CaO_{(s)}} = -151.8 \text{ kcal/mole} \; ?$$

A-23 $\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$$42.6 \text{ kcal} = [(1 \text{ mole})(-94.0 \text{ kcal/mole}) + (1 \text{ mole})(-151.8 \text{ kcal/mole})] - [(1 \text{ mole})(H_{CaCO_3})]$$

$$H_{CaCO_{3(s)}} = \frac{-42.6 \text{ kcal} - 94.0 \text{ kcal} - 151.8 \text{ kcal}}{1 \text{ mole}}$$

$$= -288.4 \text{ kcal/mole}$$

R
- **a)** $\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$
- **b)** ΔH = **negative (exothermic reaction)**
- **c)** ΔH = **positive (endothermic reaction)**
- **d)** $\Delta H_{(forward)} = -\Delta H_{(reverse)}$

S-3 How is the enthalpy of a compound determined? The enthalpy of a compound is set equal to the enthalpy change of the reaction for the formation of the compound from its pure elements This is called the heat of formation

$$A + B \rightarrow AB$$

$$\Delta H_f = \text{heat of formation} = H_{AB}$$

Q-24 From the definition of enthalpy of a compound, what can be said about the enthalpy of a pure element?

A-24 $A + B \rightarrow AB$

$\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = H_{AB} - H_A - H_B$

$\Delta H = \text{heat of formation} = \Delta H_f$

$\Delta H_f = H_{AB}$

Therefore, $H_A = -H_B$

The only way this expression can always be valid is for both H_A and H_B to be equal to zero Thus, the enthalpy of an element in its standard state is by convention equal to zero. The pure elements are taken as reference states

Q-25 The enthalpy change for the reaction

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

is equal to -94 0 kcal What is the enthalpy of CO_2?

A-25 $\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(1\text{ mole})(H_{CO_2})] - [(1\text{ mole})(H_C) + (1\text{ mole})(H_{O_2})]$

$H_C = H_{O_2} = 0$

$H_{CO_2} = \dfrac{\Delta H}{1\text{ mole}} = \Delta H_f = -94\ 0\text{ kcal/mole}$

Q-26 The enthalpy change for the reaction

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$$

is equal to -17 9 kcal What is the enthalpy of CH_4?

A-26 $\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(1\text{ mole})(H_{CH_4})] - [(2\text{ mole})(H_{H_2}) + (1\text{ mole})(H_C)]$

$H_{H_2} = H_C = 0$

$H_{CH_{4(g)}} = \dfrac{\Delta H}{1\text{ mole}} = \Delta H_f = -17\ 9\text{ kcal/mole}$

Q-27 What is the enthalpy change for the reaction

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Cl_{2(g)} = HCl_{(g)}$$

if $\Delta H_f = H_{HCl} = -22\ 1$ kcal/mole?

A-27 $\Delta H = \Sigma nH_{(p)} - \Sigma nH_{(r)}$

$\Delta H = [(1\ \text{mole})(H_{HCl})] - [0 + 0]$

$H_{HCl} = \Delta H_f = -22\ 1\ \text{kcal/mole}$

$\Delta H = (1\ \text{mole})(-22\ 1\ \text{kcal/mole})$

$= -22\ 1\ \text{kcal}$

Q-28 What is the enthalpy change for the reaction

$CH_{4(g)} + Cl_{2(g)} = CH_3Cl_{(g)} + HCl_{(g)}$

if $\Delta H_{f(CH_4)} = -17\ 9$ kcal mole

$\Delta H_{f(CH_3Cl)} = -20\ 0$ kcal mole

$\Delta H_{f(HCl)} = -22\ 0$ kcal mole ?

A-28 $\Delta H = \Sigma n\Delta H_{f_{(p)}} - \Sigma n\Delta H_{f_{(r)}}$

$\Delta H = [(1\ \text{mole})(\Delta H_{f_{(CH_3Cl)}}) + (1\ \text{mole})(\Delta H_{f_{(HCl)}})] - [(1\ \text{mole})(H_{(Cl_2)}) + (1\ \text{mole})(\Delta H_{f_{(CH_4)}})]$

$\Delta H = [(1\ \text{mole})(-20\ 0\ \text{kcal/mole}) + (1\ \text{mole})(-22\ 0\ \text{kcal/mole})] - [(1\ \text{mole})(0) + (1\ \text{mole})(-17\ 9\ \text{kcal mole})]$

$\Delta H = -24\ 1$

Q-29 What is the enthalpy change for the reaction

$C_2H_6O_{(\ell)} + 3O_{2(g)} \quad 2CO_{2(g)} + 3H_2O_{(g)}$

if $\Delta H_{f(C_2H_6O)}$ -66 3 kcal mole

$\Delta H_{f(CO_2)}$ -94 0 kcal mole

$\Delta H_{f(H_2O)}$ - -68.3 kcal mole ?

A-29 $\Delta H = \Sigma n\Delta H_{f_{(p)}} - \Sigma n\Delta H_{f_{(r)}}$

$\Delta H = [(2\ \text{moles})(\Delta H_{f_{(CO_2)}}) + (3\ \text{moles})(\Delta H_{f_{(H_2O)}})] - [(3\ \text{moles})(H_{(O_2)}) + (1\ \text{mole})(\Delta H_{f_{(C_2H_6O)}})]$

$\Delta H = [(2\ \text{moles})(-94\ 0\ \text{kcal/mole}) + (3\ \text{moles})(-68.3\ \text{kcal/mole})] - [0 + (1\ \text{mole})(-66.3\ \text{kcal mole})]$

$\Delta H = -326\ 6\ \text{kcal}$

Q-30 The ΔH_f for a compound depends on the temperature at which the reaction takes place In tables of thermodynamic data (see Table I), the heats of formation are given for the compound at 25 C and 1 atm pressure. This is called the <u>standard heat of formation</u>, ΔH_f .

What is the enthalpy change at 25 C for the reaction

$2N_2O + 3O_2 - 2N_2O_4$

if $\Delta H_f^{\circ}{}_{(N_2O)}$ - 19.5 kcal mole

$\Delta H_f^{\circ}{}_{(N_2O_4)}$ 2.3 kcal mole ?

A-30 $\Delta H = \Sigma n \Delta H_{f(p)} - \Sigma n \Delta H_{f(r)}$

at 25°C $\quad \Delta H_f = \Delta H_f^\circ$

$\Delta H = [(2 \text{ moles})(\Delta H^\circ_{f_{(N_2O_4)}})] - [(3 \text{ moles})(H_{(O_2)}) + (2 \text{ moles})(\Delta H^\circ_{f_{(N_2O)}})]$

$\Delta H = [(2 \text{ moles})(2\ 3 \text{ kcal/mole})] - [0 + (2 \text{ moles})(19\ 5 \text{ kcal/mole})]$

$\Delta H = -34\ 4 \text{ kcal} = \Delta H^\circ$

(ΔH° is the enthalpy change for the reaction at standard conditions, 1 atm pressure and 25°C)

Q-31 What is the enthalpy change at 25°C for the reaction

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

if $\Delta H^\circ_{f_{(C_2H_4)}} = 12\ 5$ kcal/mole

$\Delta H^\circ_{f_{(C_2H_6)}} = -20\ 2$ kcal/mole ?

A-31 $\Delta H^\circ = \Sigma n \Delta H^\circ_{f_{(p)}} - \Sigma n \Delta H^\circ_{f_{(r)}}$

$\Delta H^\circ = [(1 \text{ mole})(-20\ 2 \text{ kcal/mole})] - [(1 \text{ mole})(0) + (1 \text{ mole})(12\ 5 \text{ kcal/mole})]$

$\Delta H^\circ = -32\ 7$ kcal

Q-32 Consider the reaction for the transition of carbon in the diamond form to carbon in the graphite form

$$C_{(diamond)} \rightarrow C_{(graphite)}$$

$\Delta H^\circ = -453\ 5$ cal

From an energy point of view alone, which form of carbon is more stable at 25°C?

A-32 Graphite

$\Delta H^\circ = H^\circ_{C_{(graphite)}} - H^\circ_{C_{(diamond)}}$

Since ΔH° is negative for the reaction, $H_{C_{(diamond)}}$ is greater than $H_{C_{(graphite)}}$. Therefore, the graphite form is at lower energy making it more stable

Q-33 The decomposition of hydrogen peroxide into its constituent elements according to the reaction

$$H_2O_{2(\ell)} \rightarrow H_{2(g)} + O_{2(g)}$$

is endothermic by 44.9 kcal/mole What conclusion can be made about the stability of hydrogen peroxide with respect to the elements?

A-33 Since heat is necessary to convert hydrogen peroxide into the elements, hydrogen peroxide is energetically <u>more stable</u> with respect to the elements

Q-34 The decomposition of hydrogen peroxide by the reaction

$$H_2O_{2(\ell)} \rightarrow H_2O_{(\ell)} + \tfrac{1}{2}O_{2(g)}$$

is exothermic by 23 4 kcal/mole What conclusion can be made about the stability of hydrogen peroxide with respect to decomposition into water and oxygen?

A-34 Since heat is given off when hydrogen peroxide decomposes into water and oxygen, hydrogen peroxide is energetically <u>less stable</u> with respect to the decomposition products.

Q-35 From a consideration of the last two problems, what information is needed to say whether a substance is stable or unstable?

A-35 It is useful to talk about stability only in terms of the possible decomposition products

Q-36 The enthalpies of formation for SO_2 and NO_2 are -71 0 kcal/mole and +8 1 kcal/mole, respectively Which compound is more stable with respect to the elements? Why?

A-36 SO_2 The reaction for the decomposition of SO_2 is endothermic by 71 0 kcal/mole while the decomposition of NO_2 is exothermic by 8 1 kcal/mole For an endothermic reaction, $\Delta H = +$ The products are at a higher energy than the reactants, therefore, the reactants are more stable

Q-37 The enthalpies of formation for CaO and BaO are -151 8 kcal/mole and -133 5 kcal/mole, respectively Which compound is more stable with respect to the elements? Why?

A-37 CaO The reaction for the decomposition of CaO into its elements is endothermic by 151 8 kcal/mole while the decomposition of BaO into its elements is endothermic by only 133.5 kcal/mole Thus, more energy is released in the formation of CaO, resulting in a lower energy (more stable) product

Q-38 Given the following standard enthalpies of formation

$\Delta H^\circ_{f(O_3)(g)}$ = +34 0 kcal/mole

$\Delta H^\circ_{f(CO_2)(g)}$ = -94 0 kcal/mole

$\Delta H^\circ_{f(NH_3)(g)}$ = -11 04 kcal/mole

$\Delta H^\circ_{f(HI)(g)}$ = +6 2 kcal/mole ,

arrange the compounds in the order of <u>increasing</u> stability with respect to decomposition into their elements

A-38 least stable → most stable

O_3, HI, NH_3, CO_2

Q-39 Which of the two isomers of butane (C_4H_{10}) is more stable at 25°C?

isomer	ΔH°_f
n-butane ($CH_3CH_2CH_2CH_3$)	-29 8 kcal mole
isobutane ($CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$)	-31 4 kcal mole

A-39 Isobutane It has the higher negative value for enthalpy of formation

Q-40 Consider the reaction

n-butane → isobutane .

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic? How does your answer confirm the relative stabilities of these two compounds?

A-40 $\Delta H^\circ = \Sigma n\Delta H^\circ_{f(p)} - \Sigma n\Delta H^\circ_{f(r)}$

$\Delta H^\circ = [(1 \text{ mole})(-31.4 \text{ kcal/mole})] - [(1 \text{ mole})(-29.8 \text{ kcal/mole})]$

$\Delta H^\circ = -31.4 - (-29.8) = -1.6 \text{ kcal}$

The reaction is exothermic, thus, isobutane is at lower energy and is more stable

Q-41 Which isomer of pentane (C_5H_{12}) is the most stable at 25°C in terms of energy only?

isomer	ΔH_f
n-pentane ($CH_3CH_2CH_2CH_2CH_3$)	-35.0 kcal/mole
neopentane ($(CH_3)_4C$)	-39.7 kcal/mole
isopentane ($CH_3CH_2CH(CH_3)_2$)	-36.9 kcal/mole

A-41 Neopentane. This isomer has the lowest enthalpy value

R

a) $\Delta H^\circ_{f(AB)}$ **= standard enthalpy of formation at 25°C and one atmosphere pressure**

= $H^\circ_{(AB)}$

b) $H^\circ_{(element)}$ **= 0 (by convention)**

c) $\Delta H^\circ = \Sigma n\Delta H^\circ_{f(products)} - \Sigma n\Delta H^\circ_{f(reactants)}$

d) Superscript zero indicates standard state (one atmosphere and 25°C).

S-4 If a reaction can be carried out by a series of steps, the overall enthalpy change is the sum of the enthalpy changes of the individual steps. In mathematical terms this becomes

$$A + B \rightarrow C \qquad \Delta H_1$$
$$C + D \rightarrow E \qquad \Delta H_2$$
$$A + B + D \rightarrow E \qquad \Delta H_3 \qquad \Delta H_3 = \Delta H_1 + \Delta H_2$$

This relationship is known as <u>Hess'</u> Law

Q-42 Consider two reactions, both of which produce C from A and B but which differ by the intermediate formed

1) $A + B \rightarrow Q \qquad Q \rightarrow C$
2) $A + B \rightarrow R \qquad R \rightarrow C$

Will the enthalpy change for reaction 1) be the same as the enthalpy change for reaction 2)?

A-42 Yes. The enthalpy change by either path must be identical since the overall reaction is the same.

Q-43 Calculate the enthalpy change for the reaction

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H_1$$

from the enthalpy changes for the reactions

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H_2 = -94.0 \text{ kcal}$$
$$CO_{(g)} \rightarrow \tfrac{1}{2}O_{2(g)} + C_{(s)} \quad \Delta H_3 = +26.4 \text{ kcal}$$

A-43
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2$$
$$CO_{(g)} \rightarrow \tfrac{1}{2}O_{2(g)} + C_{(s)} \qquad \Delta H_3$$
$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2 + \Delta H_3$$
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$
$$= -94.0 + 26.4$$
$$= -67.6 \text{ kcal}$$

Q-44 Calculate the enthalpy change for the reaction
$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_1$$
from the ΔH changes for the reactions
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2 = -94.0 \text{ kcal}$$
$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_3 = -26.4 \text{ kcal}$$
(Hint Equations can be subtracted as well as added)

A-44
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2$$
$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_3$$
The overall equation can be obtained by subtracting equation two from the first equation
$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2 - \Delta H_3$$
$$\Delta H_1 = \Delta H_2 - \Delta H_3$$
$$= -94.0 - (-26.4)$$
$$= -67.6 \text{ kcal}$$

Q-45 Compute the ΔH of the reaction
$$C_{(s)} + H_2O_{(\ell)} \rightarrow H_{2(g)} + CO_{(g)}$$
from the enthalpy changes of the reactions
$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_1 = -26.4 \text{ kcal}$$
$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \qquad \Delta H_2 = -57.8 \text{ kcal}$$

A-45 By subtracting the second equation from the first, the desired reaction is obtained.
$$\Delta H = \Delta H_1 - \Delta H_2$$
$$= -26.4 - (-57.8)$$
$$= +31.4 \text{ kcal}$$

Q-46 For the reaction
$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H = -26.4 \text{ kcal}$$
What is the enthalpy change for the reaction
$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)} \; ?$$

A-46
$$\Delta H = \frac{-26.4 \text{ kcal}}{\cancel{\text{mole}} \text{ of CO formed}} \Bigg| \, 2 \, \cancel{\text{mole}}$$
$$\Delta H = -52.8 \text{ kcal}$$

Q-47 Find ΔH for the reaction
$$Mg_{(s)} + 2HCl_{(g)} \rightarrow MgCl_{2(s)} + H_{2(g)}$$
from
$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)} \qquad \Delta H_1 = -153.2 \text{ kcal}$$
$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)} \qquad \Delta H_2 = -22.1 \text{ kcal.}$$

A-47 In order to obtain the desired reaction the second equation must be multiplied by two and subtracted from the first.
$$\Delta H = \Delta H_1 - 2(\Delta H_2)$$
$$= -153.2 - 2(-22.1)$$
$$= -109.0 \text{ kcal}$$

Q-48 Find the enthalpy of methane (CH_4) from

1) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$
$\Delta H = -191.8$ kcal

2) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -94.0$ kcal

3) $H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H = -57.8$ kcal

(Hint $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$
$\Delta H_f = H_{CH_4}$)

A-48 The desired reaction can be obtained by doubling reaction 3) and subtracting the first reaction from the sum of the last two

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ $\Delta H = 2(-57.8)$

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -94.0$

$-(CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}) - (\Delta H = -191.8)$

Adding these yields

$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$

$H_{CH_4} = \Delta H_f = \frac{\Delta H}{\text{mole}}$

$= 2(-57.8) - 94.0 - (-191.8)$

$= -17.8$ kcal/mole

Q-49 Calculate the enthalpy (heat of formation) for ethyl alcohol (C_2H_6O) from the enthalpy of combustion of ethyl alcohol

1) $C_2H_6O_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$ $\Delta H = -326.7$ kcal

2) $\frac{1}{2}O_{2(g)} + H_{2(g)} \rightarrow H_2O_{(\ell)}$ $\Delta H = -68.3$ kcal

3) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -94.0$ kcal

A-49 The desired reaction can be obtained by adding three times the second reaction to two times the third reaction and subtracting the first reaction

$\frac{3}{2}O_{2(g)} + 3H_{2(g)} \rightarrow 3H_2O_{(\ell)}$ $\Delta H = 3(-68.3)$

$2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}$ $\Delta H = 2(-94.0)$

$-(C_2H_6O_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}) - (\Delta H = -326.7)$

This gives.

$2C_{(s)} + \frac{1}{2}O_{2(g)} + 3H_{2(g)} \rightarrow C_2H_6O_{(\ell)}$

$H_{C_2H_6O} = \Delta H_f = \frac{\Delta H}{1 \text{ mole}}$

$= 3(-68.3) + 2(-94.0) - (-326.7)$

$= -66.2$ kcal/mole

Q-50 Combustion of diborane, B_2H_6, proceeds according to the equation

$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(g)} + 3H_2O_{(g)}$,

and 464 kcal are liberated per mole of B_2H_6. Combustion of boron metal also proceeds to the product B_2O_3 and liberates 283 kcal/mole of boron used What is the enthalpy change for the reaction

$$2B_{(s)} + 3H_{2(g)} \rightarrow B_2H_{6(g)} \quad ?$$

$(H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H = -58$ kcal)

A-50 The desired reaction can be obtained by adding the following equations

$B_2O_{3(g)} + 3H_2O_{(g)} \rightarrow 3O_{2(g)} + B_2H_{6(g)}$ $\Delta H = +464$

$2B_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow B_2O_{3(g)}$ $\Delta H = 2(-283)$

$\frac{3}{2}O_{2(g)} + 3H_{2(g)} \rightarrow 3H_2O_{(g)}$ $\Delta H = 3(-58)$

$2B_{(s)} + 3H_{2(g)} \rightarrow B_2H_{6(g)}$ $\Delta H = ?$

$\Delta H = +464 + 2(-283) + 3(-58)$

$= -276$ kcal

Q-51 The enthalpy change for the reaction $H_{2(g)} \rightarrow 2H_{(g)}$ is +104.2 kcal. This reaction is endothermic What is the absorbed energy used for in this reaction?

A-51 The energy absorbed in the reaction is used to break the H—H bond This is called the dissociation energy of the hydrogen molecule

Q-52 The enthalpy change for the reaction $O_{2(g)} \rightarrow 2O_{(g)}$ is 118 2 kcal per mole of O_2 reacted What is the dissociation energy of the O_2 molecule?

A-52 118 2 kcal/mole

Q-53 What is the dissociation energy for the chlorine molecule if H_{Cl} is 29 0 kcal/mole?

A-53 $Cl_{2(g)} \rightarrow 2Cl_{(g)}$ $\Delta H = ?$

$\Delta H = 2H_{Cl} - H_{Cl_2}$ $H_{Cl} = 29\ 0$

$H_{Cl_2} = 0$ (element in stable state)

$\Delta H = 2(29\ 0) - 0 = 58\ 0$ kcal per mole of Cl_2 reacted

Dissociation energy = 58 0 kcal/mole Cl_2

Q-54 What is the dissociation energy of HCl if

$\Delta H_{g(HCl)} = -22\ 0$ kcal/mole ?

$H_H = 52.1$ kcal/mole

$H_{Cl} = 29\ 0$ kcal/mole

A-54 $\Delta H = H_H + H_{Cl} - \Delta H_{g(HCl)}$

$= 52\ 1 + 29\ 0 - (-22\ 0)$

$= 103\ 1$ kcal/mole of HCl reacted

This is the energy necessary to break the H—Cl bond

Q-55 What is the dissociation energy of ICl if

$\Delta H_{g(ICl)}$ - 4.2 kcal/mole ?

$H_{Cl} = 29.0$ kcal mole

$H_I = 25.5$ kcal/mole

A-55 $\Delta H = H_I + H_{Cl} - \Delta H_{g(ICl)}$

$= 25\ 5 + 29\ 0 - (4\ 2)$

$= 50\ 3$ kcal/mole of ICl reacted

This is the energy necessary to break the I—Cl bond

Q-56 What is the relationship between bond energy and dissociation energy for a diatomic molecule?

A-56 They are the same

R a) $A + B \rightarrow C$ ΔH_1

$A \rightarrow Q$ ΔH_2

$Q + B \rightarrow C$ ΔH_3

Hess' Law: $\Delta H_1 = \Delta H_2 + \Delta H_3$

b) Dissociation energy for a diatomic molecule is equal to the bond energy.

c) $AB \rightarrow A + B$ ΔH = dissociation energy.

S-5 The dissociation energy and bond energy are not identical for polyatomic molecules (molecules with three or more atoms). For example, consider the H_2O molecule. One dissociation step would be

$$H_2O_{(g)} \rightarrow H_{(g)} + OH_{(g)} \qquad \Delta H = 119.9 \text{ kcal}$$

The second dissociation step would be

$$OH_{(g)} \rightarrow O_{(g)} + H_{(g)} \qquad \Delta H = 101.2 \text{ kcal}$$

The O—H bond energy would be defined as the average of these two values

$$\epsilon_{OH} = \frac{119.9 + 101.2}{2} = 110.6 \text{ kcal/mole of OH bond}$$

The dissociation energy is the energy required to break a given bond of some specific compound. Bond energy is an average value of the dissociation energies of a given bond in a series of different dissociating species.

Q-57 Calculate the C—H bond energy from the following dissociation energies:

$$CH_4 \rightarrow CH_3 + H \qquad \Delta H = 103 \text{ kcal/mole of } CH_4$$

$$CH_3 \rightarrow CH_2 + H \qquad \Delta H = 89 \text{ kcal/mole of } CH_3$$

$$CH_2 \rightarrow CH + H \qquad \Delta H = 123 \text{ kcal/mole of } CH_2$$

$$CH \rightarrow C + H \qquad \Delta H = 81 \text{ kcal/mole of CH}$$

(All species are in the gaseous state)

A-57 $CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)} \qquad \Delta H = ?$

bond energy (ϵ_{C-H}) $= \frac{\Delta H}{4}$

The above equation may be obtained by adding the four equations together. Therefore,

$$\Delta H = 103 + 89 + 123 + 81$$

$$= 396 \text{ kcal/mole}$$

$$\epsilon_{C-H} = 396/4 = 99.0 \text{ kcal/mole}$$

Q-58 The sum of the dissociation energies for C_2H_6 dissociating into its elements is 674.6 kcal/mole. With the value of ϵ_{C-H} found for methane, calculate the C—C bond energy in ethane

```
   H  H
   |  |
H—C—C—H
   |  |
   H  H
```

A-58 $C_2H_{6(g)} \rightarrow 2C_{(g)} + 6H_{(g)} \qquad \Delta H = 674.6 \text{ kcal}$

Six C—H bonds were broken: 99.0 kcal/mole for each bond. Total for six = 594 kcal/mole. Subtracting gives 674.6 - 594.0 = 80.6 kcal/mole. This equals ϵ_{C-C} or the energy to break the C—C bond.

Q-59 The sum of the dissociation energies for C_3H_8 dissociating into its elements is 952.0 kcal/mole. With the value of ϵ_{C-H} found in Q-57, calculate the C—C bond energy in

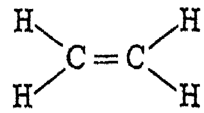
```
   H  H  H
   |  |  |
H—C—C—C—H
   |  |  |
   H  H  H
```

and compare with the value found for C_2H_6.

A-59 $C_3H_{8(g)} \rightarrow 3C_{(g)} + 8H_{(g)}$ $\Delta H = 952\ 0$ kcal

Eight C—H bonds were broken at 99 0 kcal/mole each total for 8 = 792 kcal/mole Therefore, 952 - 792 = 160 kcal/mole = energy necessary to break two C—C bonds $\epsilon_{C-C} = 160/2$ = 80 0 kcal/mole which is the energy necessary to break one C—C bond This value is approximately the same as that calculated from C_2H_6

Q-60 The sum of the dissociation energies for C_2H_4 dissociating into its elements is 544 kcal/mole With the value of ϵ_{C-H} found in Q-57, calculate the C=C bond energy in



A-60 $C_2H_{4(g)} \rightarrow 2C_{(g)} + 4H_{(g)}$ $\Delta H = 544$ kcal

Four C—H bonds were broken at 99 0 kcal/mole of each bond total for 4 = 396 kcal/mole Therefore, 544 - 396 = 148 kcal/mole = $\epsilon_{C=C}$ which is the energy necessary to break one C=C bond

Q-61 The sum of the dissociation energies for C_2H_2 dissociating into its elements is 392 kcal/mole. With the value of ϵ_{C-H} found in Q-57, calculate the $C\equiv C$ bond energy in $H-C\equiv C-H$

A-61 $C_2H_{2(g)} \rightarrow 2C_{(g)} + 2H_{(g)}$ $\Delta H = 392$ kcal

Two C—H bonds were broken for a total energy of 198 kcal/mole Therefore, $\epsilon_{C\equiv C} = 392 - 198 = 194$ kcal/mole which is the energy necessary to break one $C\equiv C$ bond.

Q-62 List the following in order of increasing bond strength. $C\equiv C$, C—C, C=C

A-62 $C-C < C=C < C\equiv C$

Q-63 What general statement can be made relating bond strength to bond order, i e , single, double, triple?

A-63 The higher the bond order the greater the bond strength.

Q-64 In the reaction $2Cl_{2(g)} + C_{(g)} \rightarrow CCl_{4(g)}$, what bonds are being made and what bonds broken?

A-64 Two Cl—Cl bonds are being broken and four C—Cl bonds are being formed.

Q-65 Show that ΔH for the reaction

$$A-A + B-B \rightarrow 2AB$$

is equal to (Σ energy of bonds being broken - Σ energy of bonds being formed)

(Hint: Write ΔH for the dissociation of each molecule.)

A-65 $A-A \rightarrow 2A \qquad \Delta H_1 = \epsilon_{A-A}$

$B-B \rightarrow 2B \qquad \Delta H_2 = \epsilon_{B-B}$

$A-B \rightarrow A+B \qquad \Delta H_3 = \epsilon_{A-B}$

Take twice the negative of the last reaction and add to the first two to get the overall enthalpy change (Hess' Law).

$$\Delta H = \Delta H_1 + \Delta H_2 - 2\Delta H_3$$
$$= \epsilon_{A-A} + \epsilon_{B-B} - 2\epsilon_{A-B}$$

Since $\epsilon_{A-A} + \epsilon_{B-B}$ represents the total energy of bonds being broken and $2\epsilon_{A-B}$ represents the total energy of bonds being formed,

$\Delta H = \Sigma$ energy of bonds being broken $- \Sigma$ energy of bonds being formed.

Q-66 Calculate the C−Cl bond energy (ϵ_{C-Cl}) if the enthalpy change for the reaction in Q-64 is -198 kcal and the ϵ_{Cl-Cl} is 57 kcal/mole

A-66 ΔH = (Σ energy of bonds being broken) - (Σ energy of bonds being formed)

$$-198 = 2(57) - (4)(\epsilon_{C-Cl})$$

$$\epsilon_{C-Cl} = \frac{-198 - 114}{-4} = 78 \text{ kcal/mole}$$

Q-67 Calculate the C≡N bond energy ($\epsilon_{C\equiv N}$) if the enthalpy change for the reaction

$$2C_{(g)} + \tfrac{1}{2}N_{2(g)} + \tfrac{3}{2}H_{2(g)} \rightarrow H-\underset{H}{\overset{H}{C}}-C\equiv N_{(g)}$$

is

$\Delta H = -322$ kcal/mole

$\epsilon_{N\equiv N} = 225$ kcal/mole

$\epsilon_{H-H} = 103$ kcal/mole

$\epsilon_{C-C} = 80$ kcal/mole

$\epsilon_{C-H} = 99$ kcal/mole

A-67 ΔH = (Σ energy of bonds broken) - (Σ energy of bonds formed)

$$-322 = \tfrac{1}{2}(225) + \tfrac{3}{2}(103) - (80 + 3(99) + \epsilon_{C\equiv N})$$

$$\epsilon_{C\equiv N} = 212 \text{ kcal/mole}$$

Q-68 Calculate the enthalpy change for the reaction

$$C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)}$$

if the bond energies are

$\epsilon_{O_2} = 117$ kcal/mole

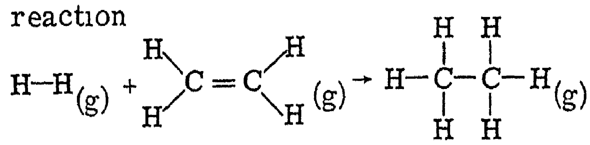
$\epsilon_{C=O} = 173$ kcal/mole .

A-68 $\Delta H = (\Sigma \epsilon_{\text{bonds broken}}) - (\Sigma \epsilon_{\text{bonds formed}})$

$= 117 - 2(173)$

$= -229$ kcal

Q-69 Calculate the enthalpy change for the reaction



if the bond energies are

$\epsilon_{H-H} = 103$ kcal/mole

$\epsilon_{C=C} = 145$ kcal/mole

$\epsilon_{C-C} = 80$ kcal/mole

$\epsilon_{C-H} = 99$ kcal/mole

A-69 $\Delta H = \epsilon_{H-H} + \epsilon_{C=C} - \epsilon_{C-C} - 2\epsilon_{C-H}$

$= 103 + 145 - 80 - 2(99)$

$= -30$ kcal

Q-70 The experimental value for the enthalpy for the reaction in Q-69 is -32.7 kcal. Why might the calculated and the experimental values differ?

A-70 The bond energies used are average bond energies. The bond energy in a specific compound may differ from the average by several kcal/mole.

Q-71 Estimate the enthalpy change for the reaction

$SiH_{4(g)} + 4HCl_{(g)} \rightarrow SiCl_{4(g)} + 4H_{2(g)}$

if the bond energies are

$\epsilon_{Si-H} = 76$ kcal/mole

$\epsilon_{H-Cl} = 103$ kcal/mole

$\epsilon_{Si-Cl} = 87$ kcal/mole

$\epsilon_{H-H} = 103$ kcal/mole.

A-71 $\Delta H = 4\epsilon_{Si-H} + 4\epsilon_{H-Cl} - 4\epsilon_{Si-Cl} - 4\epsilon_{H-H}$

$= 4(76) + 4(103) - 4(87) - 4(103)$

$= -44$ kcal

R **a) ΔH = (Σ energy of bonds being broken) - (Σ energy of bonds formed)**

b) The greater the bond order, the larger the bond energy

c) Bond energy is an average value of the dissociation energies of a given bond in a series of different dissociating species.

S-6 Another factor which determines whether a chemical reaction will take place is the change in entropy, S, of a system. Entropy is the measure of the probability of a system. The higher the probability of a system existing in a given state, the higher will be the entropy of the system.

Q-72 Consider four coins. How many ways can the coins be arranged so that all the coins will be heads or all the coins will be tails?

A-72 There is only one way to arrange the coins so that they are all heads or all tails

(1)	(2)	(3)	(4)
H	H	H	H

Q-73 How many ways can the coins be arranged so that there will be one head and three tails? Illustrate

A-73 Four

(1)	(2)	(3)	(4)
H	T	T	T
T	H	T	T
T	T	H	T
T	T	T	H

Q-74 How many ways can the coins be arranged so that there will be two heads and two tails? Illustrate.

A-74 Six

(1)	(2)	(3)	(4)
H	H	T	T
H	T	H	T
H	T	T	H
T	H	H	T
T	H	T	H
T	T	H	H

Q-75 How many ways can the coins be arranged so that there will be one tail and three heads? Illustrate

A-75 Four·

(1)	(2)	(3)	(4)
T	H	H	H
H	T	H	H
H	H	T	H
H	H	H	T

Q-76 The four coins are placed in a box. The box is shaken and a record is kept of how many heads and tails appear after each shaking This process was repeated a thousand times. Which arrangement of coins will appear the most times?

A-76 Two heads and two tails. This is called the most probable arrangement

Q-77 Which arrangement of coins has the least probability?

A-77 All heads or all tails. There is only one way of obtaining these arrangements.

Q-78 Remembering that a high probability is analogous to a high entropy, which arrangement of the coins has the greatest entropy? Why?

A-78 Two heads and two tails. This arrangement has the highest probability.

Q-79 Which arrangement of the coins has the smallest entropy? Why?

A-79 All heads or all tails. This arrangement has the lowest probability.

Q-80 The entropy is often said to be related to the disorder of a system. Consider the system of the four coins. Which arrangement has the greatest disorder?

A-80 Two heads and two tails. There are more ways to arrange the coins to get two heads and two tails than any other arrangement.

Q-81 Which arrangement of the coins has the most order?

A-81 All heads or all tails. There is only one way to obtain these arrangements.

Q-82 What is the relationship between <u>entropy</u> and <u>disorder</u> for a system?

A-82 The higher the entropy of a system, the greater is its disorder.

Q-83 A change in entropy of a system is defined as $\Delta S = S_{final} - S_{initial}$. If the four coins in a box are arranged so that they are all heads and the box is shaken, the arrangement of the coins might change to three heads and one tail or maybe two heads and two tails. What is the entropy change, ΔS, for this process? Is it positive, negative or is there no change? Why?

A-83 positive

$$\Delta S = S_{final} - S_{initial}$$

$$S_{final} > S_{initial}$$

Q-84 In the above change, does the system go to a more disordered state or a more ordered state?

A-84 A more disordered state

Q-85 What is the relationship between the change in entropy and the change in order for a system going from one state to another?

A-85 A positive entropy change is associated with a system going to a more disordered state. A negative entropy change is associated with a system going to a more ordered state.

Q-86 In the example of the coins,

4 heads → 2 heads + 2 tails

the energy of the system remains constant. (The energy of each coin is the same whether a head or tail is showing.) As long as the energy remains constant ($\Delta H = 0$), the entropy is a measure of the spontaneity of a process. If ΔS is positive, the process is spontaneous. If ΔS is negative, the process in the reverse direction is spontaneous. In the process below:

H T T T → T H H T

what is the entropy change? Is the process spontaneous?

A-86 ΔS = positive. The process is spontaneous. The entropy change can be considered as a force tending to place the system in the final state.

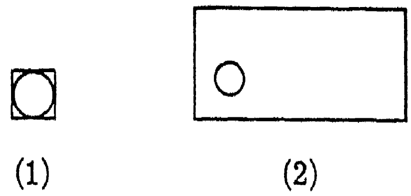
Q-87 In the process below

H T T T → T T T T

what is the entropy change? Is the process spontaneous?

A-87 ΔS = negative The process is spontaneous in the reverse direction In order for the process to occur as written, a force must be applied which overcomes the entropy force This can be done by adding energy to the system (In such a case, ΔH will no longer be zero)

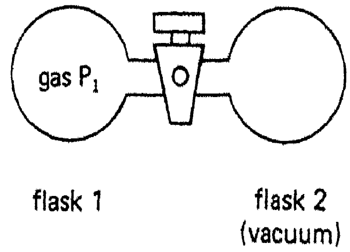
Q-88 Consider the two diagrams below



In diagram (1), a molecule is placed in a box the size of the molecule. In diagram (2) a molecule is placed in a box 9 times as large as box (1) Which system would have the greatest disorder? Why?

A-88 Diagram (2) The molecule has more space in which to move around, therefore, the system would have more disorder In diagram (1), the molecule is held in a fixed position

Q-89 The concept of entropy can be applied in the same manner to chemical systems Consider the expansion of an ideal gas from one container into an evacuated container



What happens to the gas when the stopcock is opened between the two flasks?

A-89 Gas flows from flask 1 into flask 2 until the pressure in the two flasks is equal.

Q-90 Is there any enthalpy change (ΔH) in the process? Why?

A-90 No. $\Delta H = 0$. The only process taking place is that of the molecules moving further apart. Since there are no attractions between ideal gas molecules, no energy is released or absorbed when molecules are moved further apart.

Q-91 Which state has more disorder? Why?

A-91 The final state has more disorder than the initial state. The greater disorder of the final state arises from the molecules having more volume in which to move around.

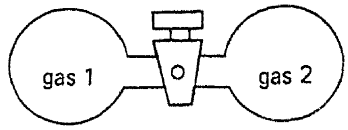
Q-92 The reason the gas expands is that the entropy change for the process is positive. The entropy change is the driving force for the process. Why is the entropy change positive for this process?

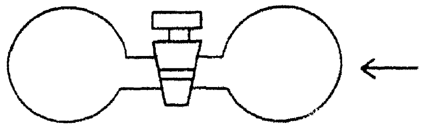
A-92 The greater the disorder, the greater is the entropy Since the disorder in the final state is greater than that of the initial state, the entropy in the final state is greater

ΔS = positive, if $S_{final} > S_{initial}$

(If the gas had not been ideal, energy would have to be added to break the forces of attraction between the molecules Therefore, two forces would be at work - an enthalpy force and an entropy force In this question only the entropy force was considered)

Q-93 Consider the following process for mixing two ideal gases





gas 1 and 2 mixed

Which state (initial or final) has the greater disorder?

A-93 The final state has more disorder There is more order if the two gases are in their own container

Q-94 What is the driving force for the above process to take place?

A-94 The change in entropy (ΔS = +)

Q-95 Consider the process of dissolving a lump of salt in a beaker of water. What is the sign of the entropy change for this process?

A-95 ΔS = positive. Final state is more disordered than initial state.

Q-96 What is the sign for the change in entropy for the freezing of liquid water?

A-96 ΔS = negative In the liquid state, water molecules are more disordered than in the ordered solid.

Q-97 What is the sign for the change in entropy for the vaporization of a liquid?

A-97 ΔS = positive In the gas state, molecules are less ordered than in the liquid state

Q-98 Consider the chemical reaction:

$$A + B \rightarrow AB$$

What would the sign for the entropy change be for the reaction?

A-98 ΔS = negative Since two molecules are combining together to form one molecule, the order of the system is increasing.

Q-99 What would be the sign for the entropy change of this reaction:

$$AB \rightarrow A + B \quad ?$$

A-99 ΔS = positive. The dissociation reaction causes more disorder in the system.

Q-100 Consider the reaction:

$$A + B \rightarrow C + D$$

What would the sign of the entropy be for this reaction?

A-100 If the entropy, S, of A, B, C, and D are all the same, ΔS would be zero. This is usually not the case. The <u>entropy</u> of a <u>given</u> <u>molecule</u> depends on the <u>motion</u> of the <u>atoms</u> in the molecule as well as the motion or <u>speed</u> of the <u>molecule</u> itself.

Q-101 Consider two dogs asleep in one kennel and two puppies playing in another kennel. In which kennel will there be the greatest disorder? Why?

A-101 The one containing the puppies will have the greatest disorder because of the greater motion of the animals

Q-102 How can the motion of a molecule be increased?

A-102 Increasing the temperature

Q-103 Since disorder is related to motion, what must entropy be dependent upon?

A-103 Temperature

Q-104 As the temperature increases, does the entropy increase or decrease? Why?

A-104 Increase More motion gives greater disorder

Q-105 At absolute zero, the entropy of all pure elements and compounds is zero How can you account for this?

A-105 At absolute zero the kinetic energy is zero and the system is rigid, making it a completely ordered system A complete lack of disorder results in zero entropy

Q-106 In order to determine the entropy change for a reaction such as $A + B \rightarrow C + D$, the entropy of each compound must be known at the temperature at which the reaction is being carried out The change in entropy is determined from the relationship

$$\Delta S = \Sigma nS_{(products)} - \Sigma nS_{(reactants)}$$

If the entropies of the reactants and products were

$$S^\circ_A = 20 \text{ cal/mole-deg}$$
$$S^\circ_B = 25 \text{ cal/mole-deg}$$
$$S^\circ_C = 18 \text{ cal/mole-deg}$$
$$S^\circ_D = 23 \text{ cal/mole-deg},$$

determine the change in entropy for conversion of one mole of A and one mole of B into one mole of C and one mole of D. S° refers to the entropy at the standard conditions of 25°C and one atm pressure. (See Table II.)

A-106 For conversion of one mole of A and one mole of B into one mole of C and one mole of D,

$$\Delta S^\circ = \Sigma nS^\circ_p - \Sigma nS^\circ_r$$

$$\Delta S^\circ = [(1 \text{ mole})(18 \text{ cal/mole-deg}) + (1 \text{ mole})(23 \text{ cal/mole-deg})] - [(1 \text{ mole})(20 \text{ cal/mole-deg}) + (1 \text{ mole})(25 \text{ cal/mole-deg})]$$

$\Delta S^\circ = -4$ cal/deg.
(ΔS° is the entropy change for the reaction at standard conditions, 1 atm pressure and 25°C.)

Q-107 Provided that the enthalpy change (ΔH) for the above reaction is zero, would the reaction be expected to be spontaneous to the left or right?

A-107 $\Delta S^\circ = -4$ cal/deg

It is spontaneous in the reverse direction or to the left

Q-108 What is the entropy change for the reaction

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$$

at 25°C if

$S^\circ_{H_2}$ = 31 2 cal/mole-deg

$S^\circ_{O_2}$ = 49 0 cal/mole-deg

$S^\circ_{H_2O}$ = 45 1 cal/mole-deg

A-108 For the conversion of one mole of H_2 and one half mole of O_2 into one mole of H_2O,

$\Delta S^\circ = \Sigma nS^\circ_p - \Sigma nS^\circ_r$

ΔS° = [(1 mole)(45 1 cal/mole-deg)] - [(1 mole)(31.2 cal/mole-deg) + [($\tfrac{1}{2}$ mole)(49 0 cal/mole-deg)]

ΔS° = -10 6 cal/deg

(The units for this answer would also be cal/deg per mole of H_2O formed)

Q-109 Provided that the enthalpy change (ΔH°) for the above reaction is zero (which it isn't), would the reaction be spontaneous as written?

A-109 No ΔS° is negative

Q-110 Ignoring the effect of ΔH on the reaction

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

and considering only entropy, S, would the reaction be expected to be spontaneous?

$S^\circ_{CaCO_{3(s)}}$ = 22 2 cal/mole-deg

$S^\circ_{CaO_{(s)}}$ = 9.5 cal/mole-deg

$S^\circ_{CO_{2(g)}}$ = 51.1 cal/mole-deg

A-110 For the conversion of one mole of $CaCO_3$ into one mole of CaO and one mole of CO_2,

$\Delta S^\circ = \Sigma nS^\circ_p - \Sigma nS^\circ_r$

ΔS° = [(1 mole)(9 5 cal/mole-deg) + (1 mole)(51.1 cal/mole-deg)] - [(1 mole)(22.2 cal/mole-deg)]

ΔS° = 38.4 cal/deg

ΔS° is positive; therefore, the reaction should be spontaneous.

Q-111 Calculate the entropy change which accompanies the formation of 1 mole of gaseous HCl from its elements at 25°C.

S°_{HCl} = 44.6 cal/mole-deg .

$S^\circ_{H_2}$ = 31.2 cal/mole-deg

$S^\circ_{Cl_2}$ = 53.3 cal/mole-deg

A-111 For the conversion of one half mole of H_2 and one half mole of Cl_2 into one mole of HCl,

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}$$

$$\Delta S^\circ = \Sigma nS^\circ_p - \Sigma nS^\circ_r$$

$$\Delta S^\circ = [(1 \text{ mole})(44\ 6 \text{ cal/mole-deg})] - [(\tfrac{1}{2} \text{ mole})(31\ 2 \text{ cal/mole-deg}) + (\tfrac{1}{2} \text{ mole})(53\ 3 \text{ cal/mole-deg})]$$

$$\Delta S^\circ = 2\ 4 \text{ cal/deg}$$

Q-112 Calculate the entropy change which accompanies the formation of 1 mole of gaseous CO_2 from its elements at 25°C

$S^\circ_{CO_2} = 51\ 1$ cal/mole-deg

$S^\circ_C = 37.8$ cal/mole-deg

$S^\circ_{O_2} = 49\ 0$ cal/mole-deg

A-112 $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$$\Delta S^\circ = \Sigma nS^\circ_p - \Sigma nS^\circ_r$$

$$\Delta S^\circ = [(1 \text{ mole})(51\ 1 \text{ cal/mole-deg})] - [(1 \text{ mole})(37.8 \text{ cal/mole-deg}) + (1 \text{ mole})(49.0 \text{ cal/mole-deg})]$$

$$\Delta S^\circ = -35.7 \text{ cal/deg}$$

Q-113 What is the entropy change for the reaction

$$2CH_{4(g)} + 2C_2H_{6(g)} \rightarrow 2C_3H_{8(g)} + 2H_{2(g)}$$

if $S^\circ_{CH_4} = 44.5$ cal/mole-deg

$S^\circ_{C_2H_6} = 54\ 8$ cal/mole-deg

$S^\circ_{C_3H_8} = 64.5$ cal/mole-deg

$S^\circ_{H_2} = 31.2$ cal/mole-deg

A-113 For the conversion of two moles of CH_4 and two moles of C_2H_6 into two moles of C_3H_8 and two moles of H_2,

$$\Delta S^\circ = \Sigma nS^\circ_p - \Sigma nS^\circ_r$$

$$\Delta S^\circ = [(2 \text{ moles})(64.5 \text{ cal/mole-deg}) + (2 \text{ moles})(31.2 \text{ cal/mole-deg})] - [(2 \text{ moles})(54.8 \text{ cal/mole-deg}) + (2 \text{ moles})(44.5 \text{ cal/mole-deg})]$$

$$\Delta S^\circ = -7.2 \text{ cal/deg.}$$

[redacted]

S-7 It has been stated that the entropy change is the criterion of spontaneity provided that the enthalpy change in the process is zero. In most chemical processes the enthalpy change is not zero. Because of this, a new criterion of spontaneity will be introduced which will include both the enthalpy factor and the entropy factor. This new quantity is called the free energy, G.

$$\Delta G = \Sigma nG_{(products)} - \Sigma nG_{(reactants)}$$

Q-114 If G = H - (T)(S) (T is the absolute temperature), derive an expression for ΔG, at constant temperature, in terms of ΔH and ΔS. (Consider only one mole of each reactant and product.)

A-114

$$\Sigma G_{(p)} = \Sigma H_{(p)} - T(\Sigma S_{(p)})$$

$$\Sigma G_{(r)} = \Sigma H_{(r)} - T(\Sigma S_{(r)})$$

$$\Delta G = \Sigma G_{(p)} - \Sigma G_{(r)}$$

$$\Delta G = \Sigma H_{(p)} - \Sigma H_{(r)} - [T(\Sigma S_p) - T(\Sigma S_r)]$$

$$\Delta H = \Sigma H_{(p)} - \Sigma H_{(r)}$$

$$\Delta S = \Sigma S_{(p)} - \Sigma S_{(r)}$$

$$\Delta G = \Delta H - T\Delta S$$

Q-115 From the expression for ΔG in terms of ΔH and ΔS and a knowledge that if $\Delta H = 0$, ΔS is a measure of the spontaneity of a reaction, what should the sign of ΔG be for a spontaneous process and what should it be for a non-spontaneous process?

A-115 $\Delta G = \Delta H - T\Delta S$

$\Delta H = 0$

When ΔS is positive the reaction is spontaneous.
Therefore, ΔG is negative for a spontaneous reaction.
When ΔS is negative the reaction is non-spontaneous.
Therefore, ΔG is positive for a non-spontaneous reaction.

Q-116 It is now possible to determine the spontaneity of any chemical process regardless of whether the enthalpy change is zero or not. To determine the spontaneity of a reaction the enthalpies and entropies of both products and reactants at the same temperature, i.e., standard state, must be known.

Calculate the change in free energy, ΔG, for the following reaction at 25°C. (Remember T must be used as absolute temperature.)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ at 25°C.

	ΔH_f° (kcal/mole)	S° (cal/mole-deg)
H_2	0	31.2
O_2	0	49.0
H_2O	-57.8	45.1

(These values were obtained from Table I and Table II.)

A-116 For the conversion of one mole of H_2 and one half mole of O_2 into one mole of H_2O,

$$\Delta H^\circ = \Sigma n\Delta H^\circ_{f_{(p)}} - \Sigma n\Delta H^\circ_{f_{(r)}}$$

$$\Delta H^\circ = [(1\text{ mole})(-57.8\text{ kcal/mole})] - [0 + 0]$$

$$\Delta H^\circ = -57.8\text{ kcal}$$

$$\Delta S^\circ = \Sigma nS^\circ_p - \Sigma nS^\circ_r$$

$$\Delta S^\circ = [(1\text{ mole})(45.1\text{ cal/mole-deg})] - [(1\text{ mole})(31.2\text{ cal/mole-deg}) + (\tfrac{1}{2}\text{ mole})(49.0\text{ cal/mole-deg})]$$

$$\Delta S^\circ = -10.6\text{ cal/deg}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -57.8\text{ kcal} - (298)(-10.6\text{ cal/deg})\left(\frac{1\text{ kcal}}{1000\text{ cal}}\right)$$

$$\Delta G^\circ = -57.8\text{ kcal} + 3.2\text{ kcal}$$

$$\Delta G^\circ = -54.6\text{ kcal.}$$

It is spontaneous (ΔG° is the free energy change for the reaction at standard conditions, one atm pressure and 25°C)

Q-117 Calculate the change in free energy (ΔG°) at 25°C for the following chemical reaction

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

Is the reaction spontaneous?

(Hint Obtain information needed from Table I and Table II.)

A-117 (From Table I and II)

	ΔH°_f(kcal/mole)	S°(cal/mole-deg)
C_2H_4	12.5	52.4
H_2	0	31.2
C_2H_6	-20.24	54.8

$$\Delta H^\circ = [(1\text{ mole})(-20.24\text{ kcal/mole})] - [(1\text{ mole})(12.5\text{ kcal/mole}) + 0]$$

$$\Delta H^\circ = -32.7\text{ kcal}$$

$$\Delta S^\circ = [(1\text{ mole})(54.8\text{ cal/mole-deg})] - [(1\text{ mole})(31.2\text{ cal/mole-deg}) + (1\text{ mole})(52.4\text{ cal/mole-deg})]$$

$$\Delta S^\circ = -28.8\text{ cal/deg}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -32.7 - \frac{(298)(-28.8)}{1000}$$

$$\Delta G^\circ = -32.7 + 8.6 = -24.1\text{ kcal}$$

Spontaneous

A-118 Calculate the change in free energy at 25°C for the isomerization of isobutane into n-butane.

$$\underset{\text{isobutane}}{CH_3-\overset{\overset{\large CH_3}{|}}{CH}-CH_3} \rightarrow \underset{\text{n-butane}}{CH_3-CH_2-CH_2-CH_3}$$

	ΔH°_f(kcal/mole)	S°(cal/mole-deg)
isobutane	-31.5	70.4
n-butane	-29.8	74.1

A-118 $\Delta H^\circ = [(1\text{ mole})(-29\ 8\text{ kcal/mole})] - [(1\text{ mole})(-31\ 5\text{ kcal/mole})]$

$\Delta H^\circ = +1\ 7\text{ kcal}$

$\Delta S^\circ = [(1\text{ mole})(74\ 1\text{ cal/mole-deg})] - [(1\text{ mole})(70\ 4\text{ cal/mole-deg})]$

$\Delta S^\circ = 3\ 7\text{ cal/mole}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 1\ 7 - \frac{(298)(3\ 7)}{1000}$

$\Delta G^\circ = 1\ 7 - 1\ 1 = 0\ 6\text{ kcal}$

Spontaneous in reverse direction

Q-119 Calculate the change in free energy for the decomposition of benzene ($C_6H_{6(\ell)}$) into its elements at 25°C

A-119 (From Table I and II)

	ΔH_f°(kcal/mole)	S°(cal/mole-deg)
Benzene	11 7	41 3
H_2	0	31 2
C	0	1 37

$C_6H_{6(\ell)} \rightarrow 3H_{2(g)} + 6C_{(s)}$

$\Delta H^\circ = [0 + 0] - [(1\text{ mole})(11\ 7\text{ kcal/mole})]$

$\Delta H^\circ = -11\ 7\text{ kcal}$

$\Delta S^\circ = [(3\text{ moles})(31\ 2\text{ cal/mole-deg}) + (6\text{ moles})(1\ 37\text{ cal/mole-deg})] - [(1\text{ mole})(41\ 3\text{ cal/mole-deg})]$

$\Delta S^\circ = 60\ 5\text{ cal/deg}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -11\ 7 - \frac{(298)(60\ 5)}{1000}$

$\Delta G^\circ = -11\ 7 - 18\ 0 = -29\ 7\text{ kcal}$

Spontaneous

Q-120 Just as standard enthalpy and entropy values were given for compounds, standard free energy of formation values are given (Table III). The standard free energy of formation, ΔG_f°, for a compound is the change in free energy which accompanies the formation of one mole of the compound from its pure elements The free energy of formation of an element in its standard state is assigned a value of zero, by convention.

What is the free energy change for the reaction

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Cl_{2(g)} = HCl_{(g)}$$

if

$$G^\circ_{HCl} = -22.8\text{ kcal/mole?}$$

A-120 $\Delta G^\circ = \Sigma nG_p^\circ - \Sigma nG_r^\circ$

$\Delta G^\circ = [(1\text{ mole})(-22.8\text{ kcal/mole})] - [0 + 0]$

$\Delta G^\circ = -22\ 8\text{ kcal}$

Q-121 What is the standard free energy of formation for $HCl_{(g)}$?

A-121 Conversion of one half mole of H_2 and one half mole of Cl_2 into one mole of HCl is obtained from A-120 ΔG° for the reaction is -22.8 kcal. From the definition for standard free energy of formation,

$$\frac{\Delta G^\circ}{(1\text{ mole})} = \Delta G^\circ_{f(HCl)} = -22.8\text{ kcal/mole.}$$

Q-122 What is the relationship between free energy of a compound, G°, and the standard free energy of formation for the compound, ΔG_f°?

A-122 Identical

$$G^\circ_{AB} = \Delta G^\circ_{f_{(AB)}}$$

Q-123 Calculate the free energy change for the reaction

$$NO_2 \rightarrow NO + \tfrac{1}{2}O_2$$

at 25°C from the standard free energies of formation

$$\Delta G^\circ_{f_{(NO_2)}} = 12.4 \text{ kcal/mole}$$

$$\Delta G^\circ_{f_{(NO)}} = 20.7 \text{ kcal/mole}$$

A-123 $\Delta G^\circ = \Sigma n \Delta G^\circ_{f_{(p)}} - \Sigma n \Delta G^\circ_{f_{(r)}}$

$\Delta G^\circ = [0 + (1 \text{ mole})(20.7 \text{ kcal/mole})] - [(1 \text{ mole})(12.4 \text{ kcal/mole})]$

$\Delta G^\circ = 8.3 \text{ kcal}$

Spontaneous in reverse direction

Q-124 Calculate the standard free energy of formation for H_2O_2

The free energy change for the reaction

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

is $\Delta G^\circ = -29.9$ kcal and

$$\Delta G^\circ_{f_{(H_2O)}} = -54.6 \text{ kcal/mole}$$

A-124 $\Delta G^\circ = \Sigma n \Delta G^\circ_{f_{(p)}} - \Sigma n \Delta G^\circ_{f_{(r)}}$

$-29.9 \text{ kcal} = [0 + (1 \text{ mole})(-54.6 \text{ kcal/mole})] - [(1 \text{ mole})(\Delta G^\circ_{f_{(H_2O_2)}})]$

$\Delta G^\circ_{f_{(H_2O_2)}} = -24.7 \text{ kcal/mole}$

Q-125 The heat of vaporization (ΔH) of water at 105° is 9,590 cal/mole. The entropy change is 25.7 cal/mole-deg. What is the free energy change for the conversion of one mole of liquid water at 105°C into steam?

A-125 $\Delta G = \Delta H - T\Delta S$

$\Delta G = 9{,}590 - (378)(25.7)$

$\Delta G = 9{,}590 - 9{,}715 = -125 \text{ cal/mole}$

Spontaneous

Q-126 If the values for ΔH and ΔS were the same for the vaporization of H_2O at 90°C as they were at 105°C, what would be the value for the change in free energy for the conversion of one mole of water into vapor at 90°C?

A-126 $\Delta G = \Delta H - T\Delta S$

$\Delta G = 9{,}590 - (363)(25.7)$

$\Delta G = 9{,}590 - 9{,}329 = 261 \text{ cal/mole}$

Not spontaneous

This illustrates the effect of temperature in the entropy term.

PART II: Rates of Reactions

S-1 Using thermodynamic calculations, it is possible to determine whether products may be obtained from various reacting substances, but these calculations tell nothing about how the reactants form the products, nor the time required for them to do so. This part of the program will be concerned with the two questions,

a) How do the reactants combine to form products?
b) What is the speed of the reaction?

The speed at which a car travels is defined as the distance traveled per unit of elapsed time

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Q-1 Write a mathematical expression for speed.

A-1 $s = \frac{d}{t}$ where s is the speed, d the distance traveled, and t the elapsed time

Q-2 A car travels a distance of 120 miles in two hours. What is its speed?

A-2

$$s = \frac{d}{t}$$

$$s = \frac{120 \text{ miles}}{2 \text{ hr}} = 60 \text{ mi/hr}$$

Q-3 A man on a hike travels 3 miles in two hrs. What is his average speed in ft/sec?

(Hint: 5280 ft = 1 mi)

A-3

$$s = \frac{3 \cancel{\text{mi}}}{2 \cancel{\text{hr}}} \left| \frac{5{,}280 \text{ ft}}{1 \cancel{\text{mi}}} \right| \frac{1 \cancel{\text{hr}}}{60 \cancel{\text{min}}} \left| \frac{1 \cancel{\text{min}}}{60 \text{ sec}} \right.$$

$$s = 2\ 2 \text{ ft/sec}$$

Q-4 If a body moves with a speed of 45 cm/sec, how far will it travel in 2 min?

A-4 $d = st$

$$d = \frac{45 \text{ cm}}{\cancel{\text{sec}}} \left| \frac{60 \cancel{\text{sec}}}{1 \cancel{\text{min}}} \right| 2 \cancel{\text{min}}$$

$$= 5{,}400 \text{ cm}$$

Q-5 Rate of change is defined as the change of a quantity per unit of elapsed time. Define speed in terms of rate of change.

A-5 Speed is the rate of change of distance

S-2 Just as the distance traveled per elapsed time is the rate at which a car travels (speed), the change in concentrations of reactants and products per elapsed time as a chemical reaction proceeds is called the rate of the chemical reaction (the speed of the reaction).

Q-6 For the chemical reaction $A \rightarrow B$, it was found experimentally that the concentration of B increased by 0.20 moles/ℓ in 1 hr. What is the rate of the chemical reaction?

A-6 $\text{rate} = \dfrac{\text{change in concentration}}{\text{elapsed time}}$

$= \dfrac{0\ 20\ \text{mole}/\ell}{1\ \text{hr}}$

$= 0\ 20\ \text{mole}/\ell\text{-hr}$

Q-7 For the chemical reaction $C \rightarrow D$, the change in concentration of C in 40 sec is 0 0040 mole/ℓ What is the rate of the chemical reaction?

A-7 $\text{rate} = \dfrac{0\ 004\ \text{mole}/\ell}{40\ \text{sec}}$

$= 1\ 0 \times 10^{-4}\ \text{mole}/\ell\text{-sec}$

Q-8 For the chemical reaction $F \rightarrow G$, the initial concentration of G is 0 0 and its concentration after 70 min is 0 20 mole/ℓ What is the average rate of this chemical reaction?

A-8 $\text{rate} = \dfrac{(0\ 20 - 0.0)\ \text{mole}/\ell}{70\ \text{min}}$

$= 2.9 \times 10^{-3}\ \text{mole}/\ell\text{-min}$

Q-9 For the chemical reaction $H \rightarrow I$, the initial concentration of H is 2 7 moles/ℓ and its concentration after 2 0 hours is 1 3 mole/ℓ. What is the average rate of this reaction?

A-9 $\text{rate} = \dfrac{(2\ 7 - 1.3)\ \text{mole}/\ell}{20\ \text{hr}}$

$= 7.0 \times 10^{-1}\ \text{mole}/\ell\text{-hr}$

Q-10 For the two reactions

$A \rightarrow B$
$C \rightarrow D$

the following data were obtained·

time (hr)	conc. of A (mole/ℓ)	conc. of B (mole/ℓ)
0	0.10	0
2	0 050	0.050

time (hr)	conc of C (mole/ℓ)	conc of D (mole/ℓ)
0	0 10	0
2	0.075	0 025

Which reaction proceeds at the greatest rate? What are the rates of formation of B and D?

A-10 $A \rightarrow B$ has the greatest rate.

rate of formation of B

$= \dfrac{0.050\ \text{mole}/\ell}{2\ \text{hr}} = \dfrac{0.025\ \text{mole}}{\ell\text{-hr}}$

rate of formation of D

$= \dfrac{0.025\ \text{mole}/\ell}{2\ \text{hr}} = \dfrac{0.012\ \text{mole}}{\ell\text{-hr}}$

Q-11 Consider the reaction $A \rightarrow B$ in the preceding question. For every 0 1 mole/ℓ of B formed, what happens to the concentration of A?

A-11 The concentration of A is reduced by 0.1 mole/ℓ.

Q-12 For the reaction $A \rightarrow B$, the rate of the reaction can be followed by measuring the rate of formation of B. How else might the rate of the reaction be followed?

A-12 By measuring the rate of disappearance of A

Q-13 For a chemical reaction $A \rightarrow B$, the average rate of formation of B is 0 5 mole/ℓ-hr What is the rate of disappearance of A? (The rate of disappearance of any compound is expressed as a negative number)

A-13 Rate of disappearance of A

$= -0.5$ mole/ℓ-hr

Q-14 For the chemical reaction $2A + B \rightarrow C$, the rate of formation of C is 0 25 mole/ℓ-hr What is the rate of disappearance of A and B?

A-14 Rate of disappearance of A

$= -(2)(0.25)$ mole/ℓ-hr

$= -0.50$ mole/ℓ-hr

Rate of disappearance of B

$= -0.25$ mole/ℓ-hr

Q-15 For the chemical reaction $A \rightarrow B$, the following data were obtained

Initial conc of A (mole/ℓ)	Initial formation rate of B (mole/ℓ-hr)
0.40	0.10
0 20	0.05
0 10	0 025
0.05	0.012

What happens to the initial rate of formation of B as the initial concentration of A is decreased?

A-15 The rate of formation of B decreases.

Q-16 In the chemical reaction $A \rightarrow B$, the initial concentration of A is 0.4 mole/ℓ, and the initial rate of formation of B is 0.1 mole/ℓ-hr. What happens to the concentration of A as the reaction progresses, and what would this do to the rate of formation of B?

A-16 The concentration of A decreases. This causes the rate of formation of B to decrease

Q-17 In the chemical reaction $A \rightarrow B$ (See Q-15), the initial rate is 0.1 mole/ℓ-hr when the initial concentration of A is 0.4 mole/ℓ. When the concentration of A is halved, what happens to the rate of formation of B in terms of its original rate?

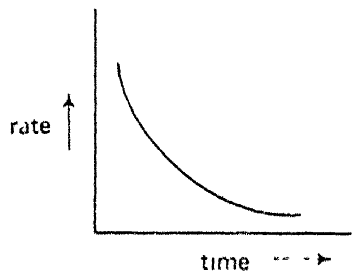
A-17 It is halved

Q-18 In general, what happens to the rate of a reaction as the reaction progresses? Why?

A-18 The rate decreases. The rate of the reaction depends on concentration of reactants As the reaction progresses the concentration of reactants decreases, causing the rate to decrease.

Q-19 Make a rough sketch of reaction rate (Y-axis) versus time (X-axis) for the reaction $A \rightarrow B$. (The general trend is all that is necessary.)

A-19



Rate decreases with time

R **Rate of reaction decreases with time.**

S-3 In the preceding section, the rates of reactions were seen to vary with concentration. The dependency of the rate of a reaction on the concentration of reactants may be expressed in mathematical terms as:

$$\text{Rate } \alpha \ [A]^{n_A}$$

where $[A]$ is the concentration (in mole/ℓ) of a reactant and n_A is a number to which the concentration of the reactant must be raised to give the observed rate.

Q-20 For the chemical reaction $A \rightarrow B$, it is found that the rate of the reaction doubles as the concentration of A is doubled. If rate $\alpha [A]^{n_A}$, what must n_A be for this reaction?

A-20 Rate $\alpha [A]$; $n_A = 1$

Q-21 For the chemical reaction $A \rightarrow C$, it is found that the rate of the reaction quadruples when the concentration of A is doubled. Write this dependency in mathematical terms. That is, if rate $\alpha [A]^{n_A}$, what must n_A be?

A-21 Rate $\alpha [A]^{n_A}$

Assume that rate = 1, when A = 1

$$1 \ \alpha [1]^{n_A}$$

When A is doubled (A = 2), the rate is quadrupled (rate = 4):

$$4 \ \alpha [2]^{n_A}$$

In order for both expressions to be valid, n_A must be equal to 2.

Therefore, rate $\alpha [A]^2$.

Q-22 For the chemical reaction $A \rightarrow D$, it is found that the rate of the reaction increases by a factor of 8 when the concentration of A is doubled. If rate $\alpha [A]^{n_A}$, what must n_A be for this reaction?

A-22 Rate $\alpha [A]^{n_A}$

Assume rate = 1, when A = 1

$$1 \ \alpha [1]^{n_A}$$

When A is doubled (A = 2), the rate is increased by a factor of 8 (rate = 8):

$$8 \ \alpha [2]^{n_A}$$

In order for both expressions to be valid, n_A must be equal to 3.

Therefore, rate $\alpha [A]^3$.

Q-23 For the chemical reaction $B \rightarrow C$, it is found that the rate of the reaction triples when the concentration of B is increased 9 times. If rate $\alpha [B]^{n_B}$, what must n_B be for the reaction?

A-23 Rate $\alpha [B]^{n_B}$

Assume rate = 1, when B = 1

$$1 \alpha [1]^{n_B}$$

When B is increased 9 times (B = 9) the rate is tripled (rate = 3)

$$3 \alpha [9]^{n_B}$$

In order for both expressions to be valid, n_B must be equal to $\frac{1}{2}$

Therefore,

$$\text{rate } \alpha [B]^{\frac{1}{2}}$$

R Rate of reaction is proportional to the concentration raised to the proper power.

$$\text{rate } \alpha [A]^{n_A}$$

S-4 The power to which the concentration of a given component must be raised in order to give the correct mathematical expression, is called the <u>order</u> of that component in the reaction

Q-24 For the chemical reaction A → C, it has been found that the rate of the reaction may be expressed as:

$$\text{rate } \alpha [A]^2$$

What is the order of A in this reaction?

A-24 2nd order; $n_A = 2$

Q-25 For the chemical reaction A → D, it has been found that the rate of the reaction may be expressed as:

$$\text{rate } \alpha [A]^3$$

What is the order of A in this reaction?

A-25 3rd order, $n_A = 3$

Q-26 For the chemical reaction A → E, it is found that the rate of the reaction doubles when the concentration of A is quadrupled. What is the order of A in this reaction?

A-26 Rate $\alpha [A]^{n_A}$

Assume A = 1, when rate = 1

$$1 \alpha [1]^{n_A}$$

When A is quadrupled (A = 4), the rate is doubled (rate = 2):

$$2 \alpha [4]^{n_A}$$

In order for both expressions to be valid, n_A must be equal to $\frac{1}{2}$. Therefore, the order of A is $\frac{1}{2}$

[redacted]

S-5 In most cases, the order of reactants are whole numbers and can be determined by inspection. However, for large whole numbers and non-whole numbers, logarithms should be used to determine the correct order For example, the rate of the reaction A → F increases by a factor of 5 18 when the concentration of A is tripled What is the order of A?

$$1\alpha[1]^{n_A} \quad \text{and} \quad 5\ 18\alpha[3]^{n_A}$$

Divide the second expression by the first to give

$$\frac{5\ 18\alpha[3]^{n_A}}{1\ \alpha\ [1]^{n_A}}$$

Therefore, $5.18 = [3]^{n_A}$ The two sides of the equation may be set equal to one another since the proportionality constants in the two expressions must be equal and would cancel out. Take the log of both sides

$$\log 5.18 = n_A(\log 3)$$
$$0\ 7143 = n_A(0\ 4771)$$
$$3/2 = n_A$$

Q-27 For the chemical reaction A → G, it is found that the rate of the reaction increases by a factor of 2 25 when the concentration of A is increased by a factor of 1.5. What is the order of A in this reaction?

A-27 $1\alpha[1]^{n_A}$ and $2.25\alpha[1.5]^{n_A}$

Divide second expression by first to give

$$2\ 25 = [1.5]^{n_A}$$
$$\log\ 2.25 = n_A(\log 1.5)$$
$$0.3522 = n_A(0.1761)$$
$$2 = n_A\ .$$

Second order in A.

Q-28 For the chemical reaction A → H, it is found that the rate of the reaction increases by a factor of 1.59 when the concentration of A is doubled. What is the order of A in this reaction?

A-28 $1\alpha[1]^{n_A}$ and $1.59\alpha[2]^{n_A}$

Divide second equation by first to give

$$1\ 59 = [2]^{n_A}$$
$$\log\ 1.59 = n_A(\log 2)$$
$$0.2014 = n_A(0.3010)$$
$$2/3 = n_A$$

2/3 order in A.

Q-29 For the chemical reaction A → I, it is found that the order of A in the reaction is third order. What happens to the rate of the reaction when the concentration of A is doubled?

A-29 $1\alpha[1]^3$ and $x\alpha[2]^3$

Divide second equation by first to give

$$x = [2]^3$$
$$x = 8.$$

The rate increases by a factor of 8.

Q-30 For the chemical reaction A → J, it is found that the order of A in the reaction is first order. What happens to the rate of the reaction when the concentration of A is tripled?

A-30 The rate increases by a factor of three

Q-31 If for the reaction $A \rightarrow M$, it is found that the rate of the reaction is proportional to A raised to the second power and k is the proportionality constant (called rate constant), write a mathematical equation to illustrate this (This mathematical equation is called the rate expression)

A-31 rate $= k\,[A]^2$

The proportionality constant (or rate constant) is different for each reaction

Q-32 The reaction $A \rightarrow B$ has been found to be first order with respect to A Write the rate expression for this reaction.

A-32 rate $= k\,[A]$

Q-33 The reaction $A \rightarrow C$ has been found to be third order with respect to A. Write the rate expression for this reaction.

A-33 rate $= k\,[A]^3$

Q-34 A reaction follows the rate expression

$$\text{rate} = k\,[A]$$

If the rate is expressed in terms of mole/ℓ-sec and the concentration of A is in mole/ℓ, what are the units of the first order rate constant?

A-34 mole/ℓ-sec = (k)(mole/ℓ)

$$k = \frac{1}{\text{sec}}$$

Q-35 A reaction follows the rate expression

$$\text{rate} = k\,[A]^2.$$

Expressing the rate in mole/ℓ-min and the concentration of A in mole/ℓ, what are the units of the second order rate constant?

A-35 mole/ℓ-min = (k)(mole^2/ℓ^2)

$$k = \ell/\text{mole-min}$$

Q-36 A reaction follows the rate expression

$$\text{rate} = k\,[A]^3$$

Expressing the rate in mole/ℓ-sec and the concentration of A in mole/ℓ, what are the units of the third order rate constant?

A-36 mole/ℓ-sec = (k)(mole^3/ℓ^3)

$$k = \ell^2/\text{mole}^2\text{-sec}$$

Q-37 The rate constant of a first order reaction is 2.5×10^{-6} sec^{-1}, and the initial concentration is 0 10 mole/ℓ What is the initial rate in mole/ℓ-sec?

A-37 rate $= k\,[A]$

$$\text{rate} = \frac{2.5 \times 10^{-6}}{\text{sec}} \times \frac{0.10 \text{ mole}}{\ell}$$

$$= 2\ 5 \times 10^{-7} \text{ mole}/\ell\text{-sec}$$

Q-38 The initial rate of a second order reaction is $5\ 0 \times 10^{-7}$ mole/ℓ-sec, and the initial concentration of the reacting substance is 0.20 mole/ℓ. What is the rate constant in ℓ/mole-sec?

A-38 rate = $k\,[A]^2$

$$\frac{5\ 0 \times 10^{-7}\ \text{mole}}{\ell\text{-sec}} = k \left[\frac{0\ 20\ \text{mole}}{\ell}\right]^2$$

$$k = \frac{5\ 0 \times 10^{-7}\ \text{mole}/\ell\text{-sec}}{(0\ 20)^2\ \text{mole}^2/\ell^2}$$

$$= 1\ 2 \times 10^{-5}\ \ell/\text{mole-sec}$$

Q-39 The initial rate of a 3/2 order reaction is $2\ 0 \times 10^{-5}$ mole/ℓ-sec when the initial concentration is 0 20 mole/ℓ Calculate the rate constant What is the rate of reaction after the concentration of the reactant becomes $\frac{1}{2}$ of the original?

A-39 rate = $k\,[A]^{\frac{3}{2}}$

$$2\ 0 \times 10^{-5}\text{mole}/\ell\text{-sec} = k\,[0\ 20\,\text{mole}/\ell]^{\frac{3}{2}}$$

$$k = \frac{2\ 0 \times 10^{-5}\ \text{mole}/\ell\text{-sec}}{0\ 089\ \text{mole}^{\frac{3}{2}}/\ell^{\frac{3}{2}}}$$

$$= 2\ 2 \times 10^{-4}\ \ell^{\frac{1}{2}}/\text{mole}^{\frac{1}{2}}\text{-sec}$$

When the concentration is one half of the original

$$\text{rate} = \frac{2\ 2 \times 10^{-4}\ \ell^{\frac{1}{2}}}{\text{mole}^{\frac{1}{2}}\text{-sec}} \times \frac{(0\ 10\ \text{mole})^{\frac{3}{2}}}{\ell^{\frac{3}{2}}}$$

$$= 7\ 0 \times 10^{-6}\ \text{mole}/\ell\text{-sec}$$

Q-40 In the reaction $CO_2 \rightarrow C + O_2$, 0 0276 mole/ℓ of CO_2 is used up in the first 50 seconds What is the average rate of the reaction over this period of time?

A-40

$$\text{rate} = \frac{-0\ 0276\ \text{mole}/\ell}{50\ \text{sec}}$$

$$= -5\ 5 \times 10^{-4}\ \text{mole}/\ell\text{-sec}$$

Q-41 In the reaction, $CO_2 \rightarrow C + O_2$, 0.0154 mole/ℓ of CO_2 is used up over the second 50 seconds What is the average rate of the reaction over this period of time?

A-41

$$\text{rate} = \frac{-0\ 0154\ \text{mole}/\ell}{50\ \text{sec}}$$

$$= -3.1 \times 10^{-4}\ \text{mole}/\ell\text{-sec}$$

Rate expression

$$\text{rate} = k\,[A]^{n_A}$$

where k is the rate constant, [A] concentration of A, and n_A is the order of A.

S-6 In an expression where the rate is negative (disappearance of reactant) the rate expression is written with a negative sign before the rate constant, in order that the rate constant in the rate expression always be a positive number. For example,

$$A \rightarrow B \qquad \text{rate} = -k\,[A]$$

where rate is the change in concentration of A with time.

Q-42 In the reaction $CO_2 \rightarrow C + O_2$, CO_2 is found to be first order. Write the rate expression for this reaction in terms of change in concentration of CO_2.

A-42 rate = $-k\,[CO_2]$

Q-43 In the reaction $CO_2 \rightarrow C + O_2$, the average rate of the reaction over the first 50 seconds is -0.00055 mole/ℓ-sec. If the initial concentration of CO_2 is 0.080 mole/ℓ and 0 0276 mole/ℓ of CO_2 is used up in the first 50 seconds, calculate the first order rate constant. (Assume that for the average rate, an average value of CO_2 is present.)

A-43 rate = $-k\,[CO_2]$

average rate = $\dfrac{-0.00055 \text{ mole}}{\ell\text{-sec}}$

average concentration = 0 080 - 0.0138
= 0 066 mole/ℓ

$\dfrac{-0\ 00055 \text{ mole}}{\ell\text{-sec}} = \dfrac{-k[0.066 \text{ mole}]}{\ell}$

$k = \dfrac{0.00055}{0.066} = 8\ 3 \times 10^{-3}\ \text{sec}^{-1}$

Q-44 Below is a table of data for the decomposition of dinitrogen pentoxide

$$2N_2O_5 \rightleftarrows 4NO_2 + O_2\ .$$

time (min)	concentration of N_2O_5 (mole/ℓ)
0	2 33
184	2 08
319	1 91
526	1 67
867	1 35

Determine the average rate between each interval in mole/ℓ-min.

A-44

time	$[N_2O_5]$	average rate mole/ℓ-min
0	2 33	
		1.36×10^{-3}
184	2 08	
		1.26×10^{-3}
319	1 91	
		1.16×10^{-3}
526	1.67	
		0.94×10^{-3}
867	1 35	

Q-45 Determine the rate expression for the decomposition of N_2O_5. Assume that for each average rate, an average concentration of $[N_2O_5]$ is present. (Hint. Use the data from the first and last interval)

A-45 First interval

rate = $-k\ [N_2O_5]^n$

rate = $-1\ 36 \times 10^{-3}$

$[N_2O_5]$ = 2 20 mole/ℓ

Last interval

rate = $-0\ 94 \times 10^{-3}$

$[N_2O_5]$ = 1.51 mole/ℓ

$$\frac{-1.36 \times 10^{-3} = -k\ [2.20]^n}{-0\ 94 \times 10^{-3} = -k\ [1.51]^n}$$

$1\ 45 = 1.46^n$

log 1.45 = n(log 1 46)

0 161 = n(0.164) 0.98 = n (≅1)

Therefore, rate = $-k\ [N_2O_5]$

Q-46 From the rate expression and the data from A-44, determine the rate constant for this reaction. (Calculate for each interval and take average.)

A-46 rate = $-k\ [N_2O_5]$

average $[N_2O_5]$ mole/ℓ	average rate (mole/ℓ-min)	k (min^{-1})
2 20	$1\ 36 \times 10^{-3}$	6.2×10^{-4}
2 00	$1\ 26 \times 10^{-3}$	6.3×10^{-4}
1.79	$1\ 16 \times 10^{-3}$	$6\ 5 \times 10^{-4}$
1 51	$0\ 94 \times 10^{-3}$	$6\ 2 \times 10^{-4}$

average = 6.3×10^{-4}/min

Q-47 For the chemical reaction $A + B \rightarrow C$, the rate of the reaction doubles when the concentration of A doubles, provided the concentration of B is constant. To what order does A enter into the rate expression?

A-47 rate α $[A]^{n_A}$

rate = 1 when A = 1

rate = 2 when A = 2

$$\frac{2 \; \alpha \; [2]^{n_A}}{1 \; \alpha \; [1]^{n_A}} \qquad 2 = [2]^{n_A}$$

Therefore, $n_A = 1$, first order.

Q-48 For the chemical reaction $A + B \rightarrow C$, the rate of the reaction quadruples when the concentration of B doubles, provided the concentration of A is constant. To what order does B enter into the rate expression?

A-48 rate α $[B]^{n_B}$

rate = 1 when B = 1

rate = 4 when B = 2

$$\frac{4 \; \alpha \; [2]^{n_B}}{1 \; \alpha \; [1]^{n_B}} \qquad 4 = [2]^{n_B}$$

$n_B = 2$, second order.

Q-49 Assuming that the order of reaction for A is one and B is two for the reaction $A + B \rightarrow C$, and the rate of the reaction increases by a factor of 8 when the concentration of both A and B are doubled, write the rate expression for this reaction

A-49 rate = $k\,[A]\,[B]^2$

Q-50 For the reaction $A + B \rightarrow D$, it is found that the order of A is two and the order of B is two in the rate expression By what factor will the rate increase when the concentration of both A and B are doubled?

A-50 rate = $k\,[A]^2\,[B]^2$

rate will increase by a factor of 16.

Q-51 For the chemical reaction $A + B \rightarrow E$, the following rate data were found:

a) rate doubles when concentration of B is doubled with concentration of A remaining the same;

b) rate increases by a factor of 16 when both the concentration of A and B are doubled.

What is the rate expression for this reaction?

A-51 rate = $k[A]^{n_A}\,[B]^{n_B}$

a) $$\frac{2 = \cancel{k}\;\cancel{[A]}^{n_A}\,(2)^{n_B}}{1 = \cancel{k}\;\cancel{[A]}^{n_A}\,(1)^{n_B}}$$

$2 = 2^{n_B} \qquad n_B = 1$

b) $$\frac{16 = \cancel{k}\,[2]^{n_A}\,(2)}{1 = \cancel{k}\,[1]^{n_A}\,(1)}$$

$16 = 2^{n_A}(2) \qquad 8 = 2^{n_A}$

$n_A = 3 \qquad$ rate = $k\,[A]^3\,[B]^1$

$= k\,[A]^3\,[B]$

Q-52 For the chemical reaction $A + B \rightarrow F$, the following rate data were found:

initial rate (mole/ℓ-sec)	initial conc. A (mole/ℓ)	initial conc. B (mole/ℓ)
0.02	0.5	0.5
0.08	1.0	0.5
0.16	1.0	1.0

Find the rate expression from this data.

A-52 rate $= k\,[A]^{n_A}\,[B]^{n_B}$

$$\frac{0.08 = \cancel{k}(1.0)^{n_A}\cancel{(0.5)}^{n_B}}{0.02 = \cancel{k}(0.5)^{n_A}\cancel{(0.5)}^{n_B}}$$

$4 = 2^{n_A} \qquad n_A = 2$

$$\frac{0.16 = \cancel{k(1.0)}^2\,(1.0)^{n_B}}{0.08 = \cancel{k(1.0)}^2\,(0.5)^{n_B}}$$

$2 = (2)^{n_B} \qquad n_B = 1$

Therefore, rate $= k\,[A]^2\,[B]$

A-53 rate $= k\,[A]^{n_A}\,[B]^{n_B}$

$$\frac{0.90 = \cancel{k}\,(6.0)^{n_A}\,\cancel{(3.0)}^{n_B}}{0.10 = \cancel{k}\,(2.0)^{n_A}\,\cancel{(3.0)}^{n_B}}$$

$9 = (3)^{n_A} \qquad n_A = 2$

$$\frac{0.90 = \cancel{k}\,\cancel{(6.0)}^2(6.0)^{n_B}}{0.90 = \cancel{k}\,\cancel{(6.0)}^2(3.0)^{n_B}}$$

$1 = (2)^{n_B} \qquad n_B = 0 \qquad [B]^0 = 1$

Therefore, rate $= k[A]^2$

A-54 Pick any two intervals and determine the rate

rate (mole/ℓ-hr)	average conc. (mole/ℓ)
$\dfrac{0.0896 - 0.1039}{3.15}$	0.0967
$\dfrac{0.0859 - 0.0896}{4.10 - 3.15}$	0.0878

rate $= -k\,[(CH_3)_3CBr]^{n_A}\,[H_2O]^{n_B}$

$$\frac{\dfrac{-0.0143}{3.15} = -\cancel{k}(0.0967)^{n_A}[H_2O]^{n_B}}{\dfrac{-0.0037}{0.95} = -\cancel{k}(0.0878)^{n_A}[H_2O]^{n_B}}$$

$$\frac{0.00454}{0.00390} = \frac{(0.0967)^{n_A}}{(0.0878)^{n_A}}$$

$1.16 = 1.10^{n_A} \qquad n_A = 1$

Therefore, $(CH_3)_3CBr$ is first order.

Q-53 For the chemical reaction $A + B \rightarrow G$, the following rate data were found

initial rate (mole/ℓ-sec)	initial conc A (mole/ℓ)	initial conc B (mole/ℓ)
0.10	2.0	3.0
0.90	6.0	3.0
0.90	6.0	6.0

Find the rate expression from these data

Q-54 The concentration of tert-butyl bromide as a function of time for the reaction

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

at 25°C is given in the table below.

time (hr)	conc of $(CH_3)_3CBr$ (mole/ℓ)
0	0.1039
3.15	0.0896
4.10	0.0859
6.20	0.0776
8.20	0.0701
10.0	0.0639
13.5	0.0529

What is the order of $(CH_3)_3CBr$ in the rate expression? (H_2O is a solvent. Its concentration remains approximately the same.)

Q-55 The following table gives the rates of a reaction between A and B, for various concentrations of both A and B. Deduce the order of each reactant and the rate constant k.

initial conc. [A] (mole/ℓ)	initial conc [B] (mole/ℓ)	-initial rate (mole/ℓ-sec)
2.3×10^{-4}	3.1×10^{-5}	5.2×10^{-4}
4.6×10^{-4}	6.2×10^{-5}	4.16×10^{-3}
9.2×10^{-4}	6.2×10^{-5}	1.664×10^{-2}

A-55 rate = $-k\,[A]^{n_A}\,[B]^{n_B}$

$$\frac{-4.16 \times 10^{-3}}{-1.66 \times 10^{-2}} = \frac{-\cancel{k}(4.6 \times 10^{-4})^{n_A}\cancel{(6.2 \times 10^{-5})^{n_B}}}{-\cancel{k}(9.2 \times 10^{-4})^{n_A}\cancel{(6.2 \times 10^{-5})^{n_B}}}$$

$0.25 = 0.50^{n_A}$ $\qquad n_A = 2$

$$\frac{-5.2 \times 10^{-4}}{-4.16 \times 10^{-3}} = \frac{-\cancel{k}(2.3 \times 10^{-4})^2(3.1 \times 10^{-5})^{n_B}}{-\cancel{k}(4.6 \times 10^{-4})^2(6.2 \times 10^{-5})^{n_B}}$$

$0.125 = (1/4)(1/2)^{n_B}$ $\qquad n_B = 1$

rate $= -k\,[A]^2\,[B]^1$

$-5.2 \times 10^{-4} = -k(2.3 \times 10^{-4})^2(3.1 \times 10^{-5})$

$k = 3.2 \times 10^8\ \ell^2/\text{mole}^2\text{-sec}$

Q-56 The following results have been obtained for the reaction between triethylamine, $(CH_3CH_2)_3N$, and methyl iodide, CH_3I, in nitrobenzene solution

-initial rate (mole/ℓ-sec)	initial conc $[(CH_3CH_2)_3N]$ (mole/ℓ)	initial conc $[CH_3I]$ (mole/ℓ)
1.0×10^{-2}	0.02	0.02
2.0×10^{-2}	0.02	0.04
1.0×10^{-2}	0.01	0.04

What is the rate expression and the rate constant for this reaction?

A-56 rate = $-k\,[(CH_3CH_2)_3N]^{n_A}\,[CH_3I]^{n_B}$

$$\frac{-1.0 \times 10^{-2}}{-2.0 \times 10^{-2}} = \frac{-\cancel{k}\cancel{(0.02)}^{n_A}(0.02)^{n_B}}{-\cancel{k}\cancel{(0.02)}^{n_A}(0.04)^{n_B}}$$

$1/2 = (1/2)^{n_B}$ $\qquad n_B = 1$

$$\frac{-2.0 \times 10^{-2}}{-1.0 \times 10^{-2}} = \frac{-\cancel{k}(0.02)^{n_A}\cancel{(0.04)}}{-\cancel{k}(0.01)^{n_A}\cancel{(0.04)}}$$

$2.0 = (2)^{n_A}$ $\qquad n_A = 1$

rate $= -k\,[(CH_3CH_2)_3N]\,[CH_3I]$

$$\frac{-1.0 \times 10^{-2}\,\text{mole}}{\ell\text{-sec}} = -k\,\frac{(0.02\,\text{mole})}{\ell}\frac{(0.02\,\text{mole})}{\ell}$$

$$\frac{1.0 \times 10^{-2}}{(0.02)^2} - k = 2.5 \times 10^1\ \ell/\text{mole-sec}$$

R **Rate expression for the change in concentration of B in the reaction**

$$A + B \rightarrow C + D$$

would be

$$\text{rate} = -k\,[A]^{n_A}\,[B]^{n_B}$$

since B is decreasing, the rate is a negative number and k is always positive.

S-7 The sum of the orders of each of the various components in a reaction is called the <u>order of the reaction</u>.

Q-57 What is the order of the reaction which has the rate expression

$$\text{rate} = k\,[A]\,[B]\ ?$$

A-57 $n_A = 1$ $\qquad n_B = 1$

$n_T = n_A + n_B = 1 + 1 = 2$

second order

Q-58 What is the order of the reaction which has the rate expression

$$\text{rate} = k\,[A]\,[B]^2\ ?$$

A-58 $n_A = 1$ $\qquad n_B = 2$ $\qquad n_T = 3$

third order

Q-59 What is the order of the reaction which has the rate expression

$$\text{rate} = k\,[A]^{\frac{1}{2}}\,[B]^{\frac{3}{2}}\ ?$$

A-59 $n_A = \frac{1}{2}$ $\qquad n_B = \frac{3}{2}$ $\qquad n_T = 2$

second order

Q-60 What is the order of the reaction which has the rate expression

$$\text{rate} = k\,[A]^{\frac{3}{2}}\,[B]^{-1}\ ?$$

A-60 $n_A = \frac{3}{2}$ $n_B = -1$ $n_T = \frac{1}{2}$

one half order

Q-61 For the chemical reaction

$$A + B + C \rightarrow D,$$

it was found that doubling the concentration of A doubles the rate, doubling the concentration of B quadruples the rate, and doubling the concentration of C has no effect on the rate What is the rate expression, the order of each component, and the order of the reaction?

A-61 rate $= k\,[A]^{n_A}\,[B]^{n_B}\,[C]^{n_C}$

$$\frac{2}{1} = \frac{\cancel{k}(2)^{n_A}\,\cancel{[B]}^{n_B}\,\cancel{[C]}^{n_C}}{\cancel{k}(1)^{n_A}\,\cancel{[B]}^{n_B}\,\cancel{[C]}^{n_C}}$$

$2 = 2^{n_A}$ $n_A = 1$

$$\frac{4}{1} = \frac{\cancel{k}\,\cancel{[A]}^{n_A}\,(2)^{n_B}\,\cancel{[C]}^{n_C}}{\cancel{k}\,\cancel{[A]}^{n_A}\,(1)^{n_B}\,\cancel{[C]}^{n_C}}$$

$4 = 2^{n_B}$ $n_B = 2$

$$\frac{1}{1} = \frac{\cancel{k}\,\cancel{[A]}^{n_A}\,\cancel{[B]}^{n_B}\,(2)^{n_C}}{\cancel{k}\,\cancel{[A]}^{n_A}\,\cancel{[B]}^{n_B}\,(1)^{n_C}}$$

$1 = 2^{n_C}$ $n_C = 0$

rate $= k\,[A]\,[B]^2$

reaction order $= 1 + 2 + 0 = 3$

Q-62 For the chemical reaction

$$A + B + C \rightarrow E$$

it was found that the rate of the reaction doubled when the concentration of B was doubled, that the rate doubled when the concentrations of both A and B were doubled, and quadrupled when the concentrations of both B and C were doubled What is the rate expression, the order of each component, and the order of the reaction?

A-62 rate $= k\,[A]^{n_A}\,[B]^{n_B}\,[C]^{n_C}$

$$\frac{2}{1} = \frac{\cancel{k}\,\cancel{[A]}^{n_A}\,(2)^{n_B}\,\cancel{[C]}^{n_C}}{\cancel{k}\,\cancel{[A]}^{n_A}\,(1)^{n_B}\,\cancel{[C]}^{n_C}}$$

$2 = (2)^{n_B}$ $n_B = 1$

$$\frac{2}{1} = \frac{\cancel{k}(2)^{n_A}\,(2)^1\,\cancel{[C]}^{n_C}}{\cancel{k}(1)^{n_A}\,(1)^1\,\cancel{[C]}^{n_C}}$$

$2 = (2)^{n_A}(2)$; $1 = 2^{n_A}$; $n_A = 0$

$$\frac{4}{1} = \frac{\cancel{k}\,\cancel{[A]}^{n_A}\,(2)^1\,(2)^{n_C}}{\cancel{k}\,\cancel{[A]}^{n_A}\,(1)^1\,(1)^{n_C}}$$

$4 = (2)(2)^{n_C}$ $n_C = 1$

rate $= k\,[B]\,[C]$

reaction order $= 0 + 1 + 1 = 2$

Q-63 For the chemical reaction

$$A + 2B \rightarrow C$$

it has been found that the rate of the reaction increased by a factor of 2.82 when the concentration of A doubled and increased by 9 when the concentration of B was tripled. What is the rate expression, the order of each component, and the order of the reaction?

A-63 rate $= k\,[A]^{n_A}\,[B]^{n_B}$

$$\frac{2.82}{1} = \frac{\cancel{k}(2)^{n_A}\,\cancel{[B]}^{n_B}}{\cancel{k}(1)^{n_A}\,\cancel{[B]}^{n_B}}$$

$2.82 = (2)^{n_A}$

$\log 2.82 = n_A(\log 2)$

$$n_A = \frac{\log 2.82}{\log 2} = \frac{0.4502}{0.3010} = 1.5$$

$$\frac{9}{1} = \frac{\cancel{k}\,\cancel{[A]}^{n_A}\,(3)^{n_B}}{\cancel{k}\,\cancel{[A]}^{n_A}\,(1)^{n_B}}$$

$9 = (3)^{n_B}$ $\qquad n_B = 2$

rate $= k[A]^{\frac{3}{2}}[B]^2$

reaction order $= 3/2 + 2 = 7/2$

Q-64 The following data were observed for the reaction

$$I^- + OCl^- = Cl^- + OI^-$$

carried out in a basic solution (OH^- present).

-initial rate (mole/ℓ-sec) (disappearance of OCl^-)	initial concentrations $[I^-]$ (mole/ℓ)	$[OCl^-]$ (mole/ℓ)	$[OH^-]$ (mole/ℓ)
1.75×10^{-4}	0 002	0.002	1.00
$8\ 75 \times 10^{-5}$	0 001	0 002	1 00
4.37×10^{-5}	0.001	0.001	1.00
$8\ 75 \times 10^{-5}$	0.001	0 001	0 50

What is the rate expression, the order of the reaction, and the rate constant?

A-64 rate $= -k\,[I^-]\,[OCl^-]\,[OH^-]$

Let $I^- = A$, $OCl^- = B$, $OH^- = C$.

$$\frac{-1\ 75 \times 10^{-4}}{-8\ 75 \times 10^{-5}} = \frac{-\cancel{k}(0.002)^{n_A}\cancel{(0.002)}^{n_B}\cancel{(1.00)}^{n_C}}{-\cancel{k}(0.001)^{n_A}\cancel{(0.002)}^{n_B}\cancel{(1.00)}^{n_C}}$$

$2 = 2^{n_A}$ $\qquad n_A = n_{I^-} = 1$

$$\frac{-8.75 \times 10^{-5}}{-4.37 \times 10^{-5}} = \frac{-\cancel{k}\cancel{(0.001)}(0.002)^{n_B}\cancel{(1.00)}^{n_C}}{-\cancel{k}\cancel{(0.001)}(0.001)^{n_B}\cancel{(1.00)}^{n_C}}$$

$2 = 2^{n_B}$ $\qquad n_B = n_{OCl^-} = 1$

$$\frac{-4.37 \times 10^{-5}}{-8.75 \times 10^{-5}} = \frac{-\cancel{k}\cancel{(0.001)}\cancel{(0.001)}(1.00)^{n_C}}{-\cancel{k}\cancel{(0.001)}\cancel{(0.001)}(0.50)^{n_C}}$$

$1/2 = 2^{n_C}$ $\qquad n_C = n_{OH^-} = -1$

$$\text{rate} = \frac{-k[I^-]\,[OCl^-]}{[OH^-]}$$

order of reaction $= 1 + 1 - 1 = 1$

$$\frac{-4.37 \times 10^{-5}\ \text{mole}}{\ell\text{-sec}} = -k\,\frac{(0.001)^2\ \text{mole}^2/\ell^2)}{1.00\ \text{mole}/\ell}$$

$$\frac{4.37 \times 10^{-5}}{1.0 \times 10^{-6}} = k = 4.37 \times 10^{1}\ \text{sec}^{-1}$$

R. For a reaction with the rate expression

rate $= k\,[A]^2\,[B]\,[C]^2$

the order of the reaction is $2 + 1 + 2 = 5$

[illegible]

S-8 The molecularity of a component in a chemical reaction is the coefficient which appears before the component in the balanced chemical reaction. The molecularity and order of a component in a chemical reaction can be but are not necessarily the same.

Q-65 Give the molecularity of each reactant in the chemical reaction

$$N_2 + 3H_2 \rightarrow 2NH_3\ .$$

A-65 $N_2 = 1$; $H_2 = 3$

Q-66 Give the molecularity of each reactant in the chemical reaction

$$O_2 + C \rightarrow CO_2\ .$$

A-66 $O_2 = 1, \quad C = 1$

Q-67 Give the molecularity of each reactant in the chemical reaction

$$4NO_{2(s)} + O_{2(g)} \rightarrow 2N_2O_{5(g)}$$

A-67 $NO_2 = 4, \quad O_2 = 1$

Q-68 For the chemical reaction

$$H_2 + I_2 \rightarrow 2HI\ ,$$

the rate expression is given as

$$\text{rate} = k\,[H_2]\,[I_2]$$

What is the molecularity and order of each reactant in the equation?

A-68

reactant	order	molecularity
H_2	1	1
I_2	1	1

Q-69 For the chemical reaction

$$I^- + OCl^- \rightarrow Cl^- + OI^-\ ,$$

the rate expression is given as

$$\text{rate} = \frac{k\,[OCl^-]\,[I^-]}{[OH^-]}$$

What is the molecularity and order of each component which appears in the rate expression?

A-69

component	order	molecularity
OCl^-	1	1
I^-	1	1
OH^-	-1	0

Q-70 The decomposition of dinitrogen pentoxide, $2N_2O_5 \rightarrow 4NO_2 + O_2$, has the rate expression:

$$\text{rate} = k\,[N_2O_5].$$

What is the molecularity and order of the N_2O_5?

A-70 molecularity = 2

order = 1

Q-71 For the chemical reaction

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O\ ,$$

the rate expression is given as

$$\text{rate} = k\,[Br^-]\,[BrO_3^-]\,[H^+]^2$$

What is the molecularity and order of each reactant?

A-71

reactant	order	molecularity
Br^-	1	5
BrO_3^-	1	1
H^+	2	6

[redacted]

S-9 A chemical equation does not reveal the pathway by which a reaction occurs. The reaction pathway, called the reaction mechanism, may be clarified from the rate expression and other appropriate experimental investigations. The interpretation of a rate expression such as, rate = k [A] [B], is that in the reaction mechanism one molecule of A collides with one molecule of B to form a molecule of product. This is illustrated by the equation: $A + B \rightarrow$ product.

Q-72 Write the equation for the reaction expressed by the rate expression

$$\text{rate} = k\,[A]^2$$

A-72 $A + A \rightarrow$ product

Q-73 Write the equation for the reaction expressed by the rate expression

$$\text{rate} = k\,[A]\,[B]^2$$

A-73 $A + 2B \rightarrow$ product

(One molecule of A collides with two molecules of B to form product)

Q-74 A chemical reaction may occur in a single step or in a sequence of steps The sum of the sequence of steps must add up to the balanced chemical equation It has been found experimentally that the sequence of steps for a chemical reaction is as follows

1) $A + A \rightarrow C$
2) $C + B \rightarrow D$

What is the overall chemical equation?

A-74

$$\begin{array}{l} A + A \rightarrow C \\ \underline{C + B \rightarrow D} \\ 2A + B \rightarrow D \end{array}$$

Q-75 It has been determined experimentally that the sequence of steps for a chemical reaction is as follows

1) $A + B \rightarrow C$
2) $C + B \rightarrow D$

What is the overall chemical equation?

A-75

$$\begin{array}{l} A + B \rightarrow C \\ \underline{C + B \rightarrow D} \\ A + 2B \rightarrow D \end{array}$$

Q-76 It has been determined experimentally that the sequence of steps for a chemical reaction is as follows

1) $A + A \rightarrow D$
2) $B + B \rightarrow E$
3) $D + E \rightarrow C$

What is the overall chemical equation?

A-76

$$\begin{array}{l} A + A \rightarrow D \\ B + B \rightarrow E \\ \underline{D + E \rightarrow C} \\ 2A + 2B \rightarrow C \end{array}$$

Q-77 It has been determined experimentally that the reaction $A + B + C \rightarrow F$ occurs during the chemical reaction $2A + B + C \rightarrow D$. What other steps might occur during the reaction?

A-77

$$\begin{array}{l} 2A + B + C \rightarrow D \\ \underline{-(A + B + C \rightarrow F} \\ A \qquad\qquad \rightarrow -F + D \end{array}$$

or, $A + F \rightarrow D$

Therefore, $A + B + C \rightarrow F$
$A + F \rightarrow D$

(It should be kept in mind that this is only one possible mechanism. More experimental information is necessary to prove this.)

Q-78 It has been determined experimentally that the reaction $B + B \rightarrow C$ occurs during the chemical reaction $A + 2B \rightarrow D$. What other steps might occur during the reaction?

A-78 $B + B \rightarrow C$
$C + A \rightarrow D$

Q-79 In the sequence of steps making up a chemical reaction, one step is usually slow compared to the other steps. This is called the rate controlling step and is determined from the rate expression. If the rate expression for a chemical reaction is rate $= k[A]$, what is the rate controlling step in the chemical reaction?

A-79 $A \rightarrow Q$, where Q can be a product or an intermediate.

Q-80 A reaction proceeds by the following two steps:

$$A + B \rightarrow C$$
$$C + B \rightarrow D.$$

Which step is the rate controlling step (slow) if the rate expression is

$$\text{rate} = k[A][B]$$

and what is the overall chemical reaction?

A-80 $A + B \rightarrow C$ is rate controlling

$$\begin{array}{l} A + B \rightarrow C \\ \underline{C + B \rightarrow D} \\ A + 2B \rightarrow D \end{array}$$

(C is called a very reactive intermediate.)

Q-81 The rate expression for the chemical reaction

$$NO_2 + CO \rightarrow NO + CO_2$$

is

$$\text{rate} = k[CO][NO_2].$$

What is a mechanism for this reaction?

A-81 $NO_2 + CO \rightarrow CO_2 + NO$

This reaction apparently occurs in a single step (elementary reaction).

Q-82 The rate expression for the chemical reaction $2A + C \rightarrow F$ is

$$\text{rate} = k[A][C].$$

What is a possible mechanism for this reaction?

A-82 $A + C \rightarrow D$ slow
$D + A \rightarrow F$ fast

(D is some reactive intermediate.)

Q-83 The rate expression for the chemical reaction $A_2 + B \rightarrow C$ is

$$\text{rate} = k[A_2].$$

What is a possible mechanism for this reaction?

A-83 $A_2 \rightarrow F$ slow
$F + B \rightarrow C$ fast

(F is some reactive intermediate.)

Q-84 Given the following mechanism for a reaction

$$\begin{array}{ll} A + B \rightarrow D & \text{slow} \\ D + A \rightarrow F & \text{fast} \\ F + B \rightarrow C & \text{fast}, \end{array}$$

write the rate expression and the overall reaction.

A-84 rate = k [A] [B]

$2A + 2B \rightarrow C$

Q-85 The rate expression for the chemical reaction $A + B + 2C \rightarrow D + E$ is

rate = k [A] [C] .

What is a possible mechanism for this reaction?

A-85
$A + C \rightarrow D + F$ slow
$F + B \rightarrow G$ fast
$G + C \rightarrow E$ fast

(Many other mechanisms are possible. The correct one can be determined only by more experimentation.)

Q-86 The rate expression for the chemical reaction

$$(CH_3)_3CI + H_2O \rightarrow (CH_3)_3COH + HI$$

is

rate = k $[(CH_3)_3CI]$.

What is a possible mechanism for this reaction?

A-86
$(CH_3)_3CI \rightarrow (CH_3)_3C^+ + I^-$ slow
$(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH + H^+$ fast
$H^+ + I^- \rightarrow HI$ fast

Q-87 The rate expression for the chemical reaction $2NO_2Cl \rightarrow 2NO_2 + Cl_2$ is given as

rate = k $[NO_2Cl]$

What is a possible mechanism for this reaction? Give the rate controlling (slow) step.

A-87
$NO_2Cl \rightarrow NO_2 + Cl$ slow
$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ fast

Q-88 If the rate expression for the chemical reaction $2NO + Cl_2 \rightarrow 2NOCl$ is given as

rate = k $[NO]^2 [Cl_2]$,

what is a possible mechanism for this reaction?

A-88 $2NO + Cl_2 \rightarrow 2NOCl$ slow

Q-89 The following mechanism has been proposed for a chemical reaction:

$(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$ slow
$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ fast.

Write the rate expression and the overall reaction

A-89 rate = k $[(CH_3)_3CCl]$

$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$

Q-90 The following mechanism has been proposed for the addition of HCl to ethylene:

$H^+ + CH_2{=}CH_2 \rightarrow CH_3\overset{+}{C}H_2$ slow
$CH_3\overset{+}{C}H_2 + Cl^- \rightarrow CH_3{-}CH_2Cl$ fast.

Write the rate expression and the overall reaction.

A-90 rate = $k[H^+][CH_2{=}CH_2]$

$H^+ + CH_2{=}CH_2 + Cl^- \rightarrow CH_3CH_2Cl$

R **The slow step in a chemical reaction is called the rate controlling, or rate determining, step. This step can be determined from the rate expression.**

$$\begin{array}{lll} A + A \rightarrow C & \text{slow} & \text{rate} = k[A]^2 \\ \underline{C + B \rightarrow D} & \text{fast} & \\ 2A + B \rightarrow D & \text{overall reaction} & \end{array}$$

(C is called an intermediate.)

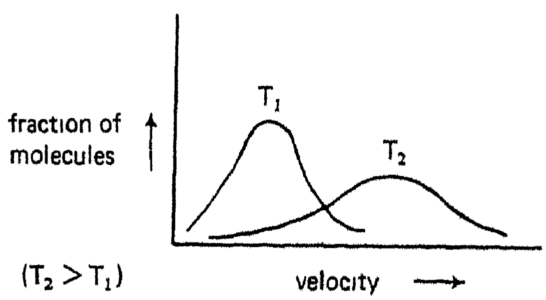
S-10 According to the kinetic molecular theory, molecules move randomly with a high velocity resulting in many collisions with each other. These collisions result in reactions between molecules provided that the colliding molecules have enough energy to cause the reaction to take place and the collisions are properly oriented. The energy needed to cause the reaction to take place is called the activation energy

Q-91 Account for the fact that rate constants for third order reactions are less than those for second order reactions

A-91 There is a greater probability for two molecules to collide than there is for three molecules to collide simultaneously

Q-92 As the temperature is increased, what happens to the velocity of molecules?

A-92 Increase in temperature causes more molecules to have a higher velocity.



Q-93 As the velocity of the molecules is increased, what happens to the energy of the molecules?

A-93 kinetic energy α T
kinetic energy α v^2
Therefore, energy increases.

Q-94 As the velocity of the molecules increases what happens to the number of collisions which a molecule makes per second?

A-94 The number of collisions per second increases.

Q-95 The minimum energy necessary to cause colliding molecules to undergo a specific reaction is called the energy of activation, E_a. As temperature increases, will the number of collisions with energy equal to or greater than the energy of activation increase or decrease?

A-95 Increase The colliding molecules have a greater kinetic energy

Q-96 Would you expect a reaction to go faster or slower at a higher temperature? Why?

A-96 Faster There are more collisions in a given time and there are a greater number of colliding molecules with energy equal to or greater than the energy of activation.

R **Reactions are the result of colliding molecules. As the temperature increases, more molecules collide with sufficient energy to cause the reaction to take place. This increases the rate of the reaction. The energy necessary to cause a reaction between colliding molecules is called the activation energy.**

S-11 The temperature dependence of the rate constant is given by the Arrhenius equation

$$k = A \quad e^{-(E_a/RT)}$$

where k is the rate constant, E_a the energy of activation, T the absolute temperature, R the ideal gas constant, and A a constant dependent on the particular reaction ($A = \rho Z$, where Z is the number of collisions that a molecule makes in a second and ρ is the fraction of collisions effective.)

Q-97 By taking the ln of both sides of the equation

$$k = A \quad e^{-(E_a/RT)}$$

obtain an expression in the form of a straight line equation ($y = a + bx$).

ln represents log to the base e

$$(\ln \ e^x = x)$$

A-97 $k \quad A \cdot e^{-(E_a/RT)}$

$\ln(k) = \ln(A) - E_a/RT$

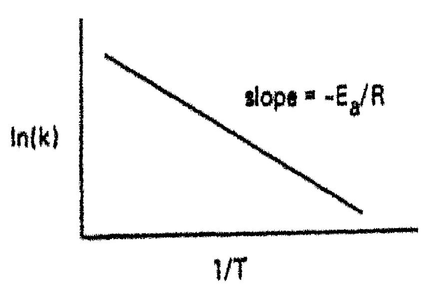
$y \quad a - bx$

$x = 1/T \qquad a = \ln(A)$

$y = \ln(k) \qquad b = -E_a/R$

Q-98 Sketch a graph of ln(k) vs 1/T for a reaction where the energy of activation, E_a, is a positive value. What is the slope equal to?

A-98



Q-99 What experimental information is necessary to determine the energy of activation for a chemical reaction? (A is an unknown constant.)

A-99 The rate constants at two or more different temperatures

Q-100 Show by use of mathematical equations how the energy of activation can be calculated from a knowledge of the rate constant at two temperatures

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A-100 at T_1 $\ln(k_1) = \ln(A) - (E_a/RT_1)$

at T_2 $\ln(k_2) = \ln(A) - (E_a/RT_2)$

Subtracting the first equation from the second gives

$$\ln\frac{(k_2)}{(k_1)} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_a = \ln\frac{(k_2)}{(k_1)}\ \frac{(RT_1T_2)}{(T_2 - T_1)}$$

$(\ln_e = 2.3 \log_{10})$

Q-101 The reaction of hexaaquochromium ion (III) and thiocyanate ion to form a complex ion,

$$Cr(OH_2)_6{}^{+3} + SCN^- \rightarrow Cr(OH_2)_5NCS^{+2} + H_2O$$

is governed by the rate law

$$\text{rate} = k\,[Cr(OH_2)_6^{+3}]\,[SCN^-]$$

The value of k is 2.0×10^{-6} ℓ/mole-sec at 14°C and 2.2×10^{-5} ℓ/mole-sec at 30°C What is the value of E_a?
(R = 1.99 cal/mole-deg)

A-101

$$E_a = \left(\frac{RT_1T_2}{T_2 - T_1}\right)\ln\frac{(k_2)}{(k_1)}$$

$$E_a = \frac{(1.99\ \text{cal})(287°)(303°)}{(\text{mole-deg})(16°)}\ln\frac{2.2\times10^{-5}}{2.0\times10^{-6}}$$

$$E_a = \frac{(1.99)(287°)(303°)}{16°}(2.3)\log\frac{2.2\times10^{-5}}{2.0\times10^{-6}}$$

$$E_a = 26{,}000\ \text{cal/mole}$$

$$E_a = \frac{26{,}000\ \text{cal}}{\text{mole}}\left|\frac{1\ \text{kcal}}{1000\ \text{cal}}\right. = \frac{26\ \text{kcal}}{\text{mole}}$$

Q-102 In many elementary books, one finds the generalization that a 10° increase in temperature causes rates of reactions to double Applied to a reaction at 295 K, what energy of activation does this correspond to?
(T_1 = 295°K, T_2 = 305°K)

A-102

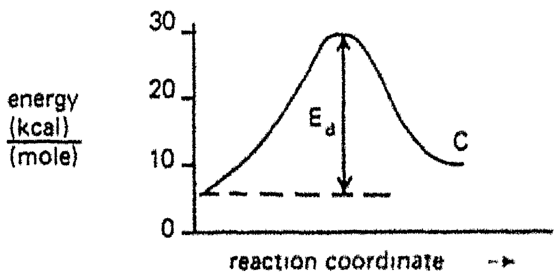
$$E_a = \frac{2.3\,RT_1T_2}{T_2 - T_1}\log\frac{(k_2)}{(k_1)}$$

$$E_a = \frac{(2.3)(1.99)(295°)(305°)\log 2}{10°}$$

$$E_a = 12{,}000\ \text{cal/mole}$$

$$E_a = \frac{12{,}000\ \text{cal}}{\text{mole}}\left|\frac{1\ \text{kcal}}{1000\ \text{cal}}\right. = \frac{12\ \text{kcal}}{\text{mole}}$$

Q-103 In the reaction A + B → C, the potential energy as a function of reaction coordinate is shown below:



The energy at A + B represents the energy of 1 mole of A and 1 mole of B molecules. The energy at C represents the energy of 1 mole of C molecules. E_a is called the activation energy. The activation energy is the difference in energy between the energy of the activated complex and the average energy of the reacting molecules. From the diagram, estimate the value for E_a and the value for ΔE of the reaction.

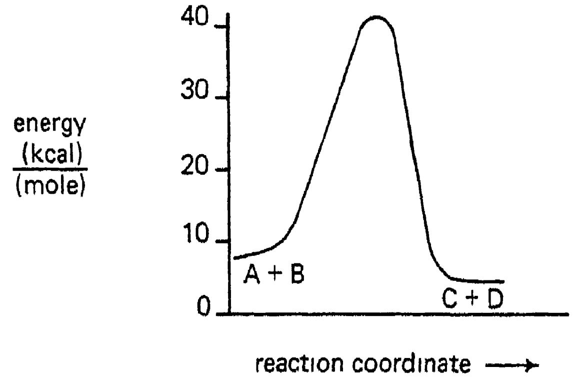
(Hint: $\Delta E = E_{product} - E_{reactant}$)

A-103 $E_a = 28 - 6 = 22$ kcal/mole

$\Delta E = E_p - E_r$

$= 11 - 6 = 5$ kcal/mole

Q-104 In the reaction $A + B \rightarrow C + D$ the potential energy as a function of reaction coordinate is shown below



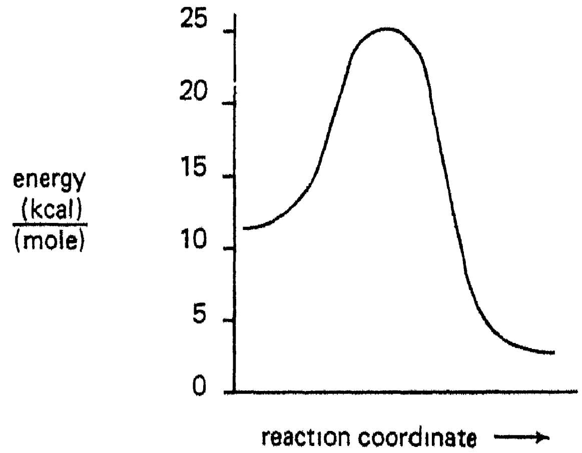
From the diagram, estimate the value for E_a and the value for ΔE of the reaction

A-104 $E_a = 42 - 8 = 34$ kcal/mole

$\Delta E = E_p - E_r$

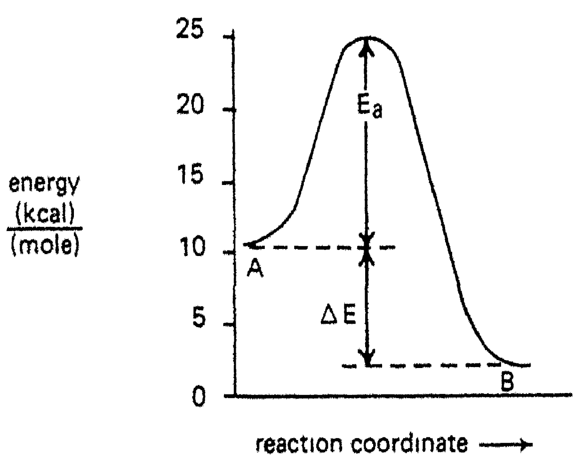
$= 4 - 8 = -4$ kcal/mole

Q-105 In the reaction $A \rightarrow B$, the potential energy as a function of reaction coordinate is shown below



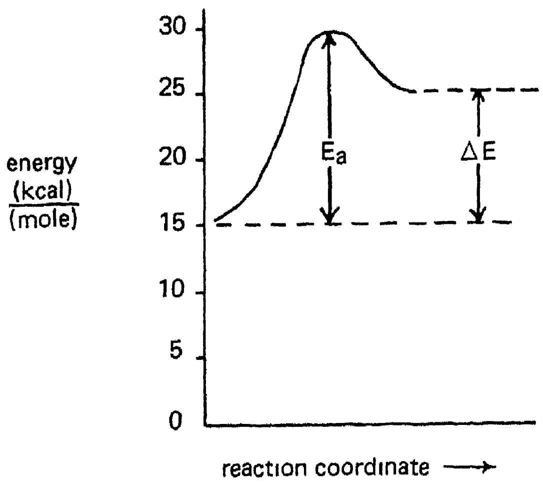
Indicate on the diagram the energy of the reactant, the product, the activation energy, and ΔE for the reaction.

A-105

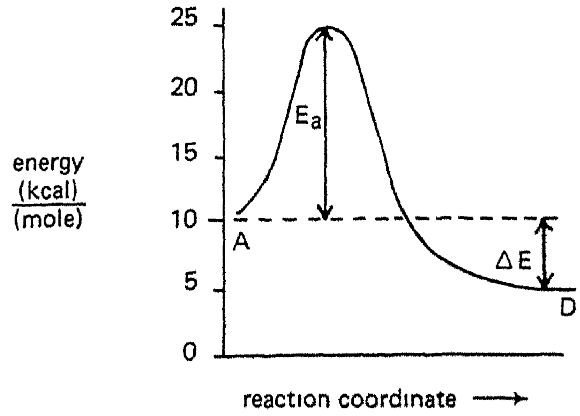


Q-106 In the reaction $A \rightarrow C$, the potential energy of A and C are 15 kcal/mole and 25 kcal/mole, respectively. Draw a diagram to illustrate the potential energy as a function of reaction coordinate The activation energy for this reaction is 15 kcal/mole.

A-106



Q-107 In the reaction $A \rightarrow D$, the potential energy as a function of reaction coordinate is shown below.



Give the E_a for the forward reaction, E_a for the reverse reaction, ΔE for the forward reaction and ΔE for the reverse reaction.

A-107 forward

$E_a = 25 - 10 = 15$ kcal/mole

$\Delta E = 4 - 10 = -6$ kcal/mole

reverse:

$E_a = 25 - 4 = 21$ kcal/mole

$\Delta E = 10 - 4 = +6$ kcal/mole

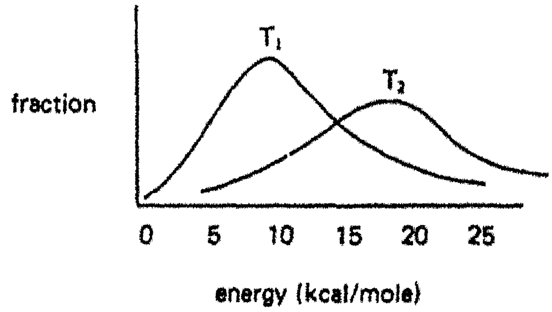
Q-108 As the temperature is increased, what happens to the average kinetic energy of a molecule?

A-108 Increases

Q-109 If the average kinetic energy increases as the temperature increases, what can be said about the fraction of molecules with kinetic energy greater than the activation energy?

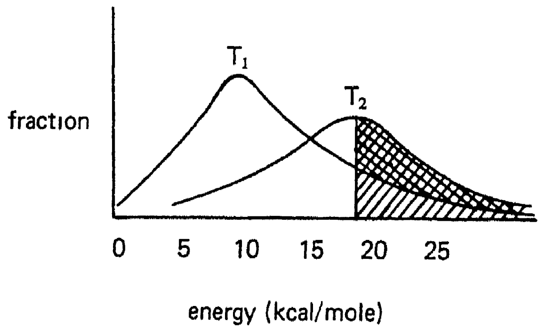
A-109 The fraction increases.

Q-110 Below is a graph of fraction of molecules vs. energy:



If the activation energy is 20 kcal/mole, show on the diagram that the fraction of molecules with energy greater than the activation energy is larger at higher temperatures.

A-110



Area darkened under T_2 curve is greater than area darkened under T_1 curve

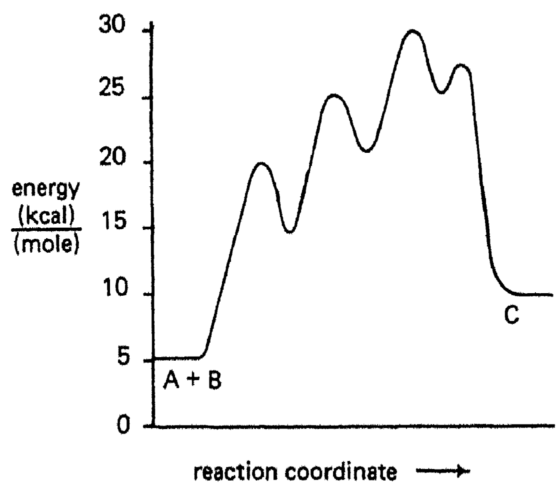
Q-111 What happens to the rate of a chemical reaction as the temperature is increased (answer in terms of the kinetic molecular theory)?

A-111 Increases As temperature increases the average kinetic energy increases, causing more molecules to have an energy greater than the activation energy. This results in more molecules crossing over the potential energy barrier, thus increasing the rate of reaction.

Q-112 What happens to the rate of the reverse reaction as the temperature is increased?

A-112 Increases. Same reasoning as A-111, i.e., the kinetic energy of the product is increased as the temperature is increased

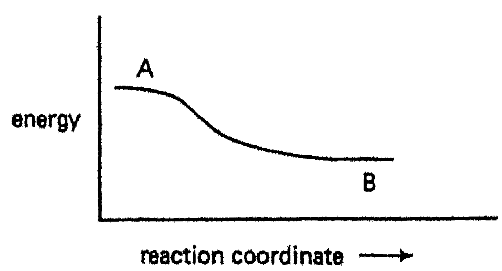
Q-113 What is the ΔE for the reaction $A + B \rightarrow C$ where the mechanism involves several kinetic steps? The potential energy diagram for such a situation might look like



A-113 $\Delta E = E_p - E_r$

$= 10 - 6 = 4$ kcal/mole

Q-114 What can you say about the existence of A if the potential energy diagram for the reaction $A \rightarrow B$ looks like



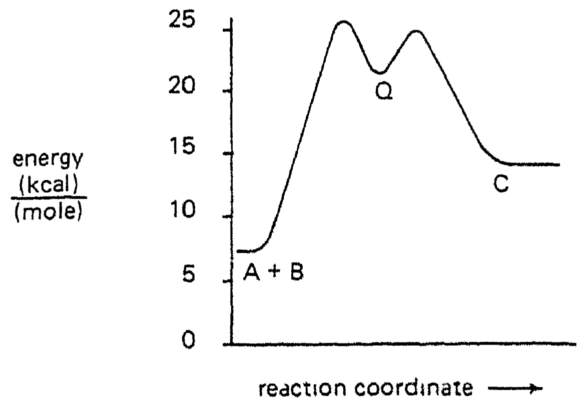
A-114 A would not exist because it would spontaneously react to form B since no energy of activation is required

Q-115 In a multistep reaction such as

$A + B \rightarrow Q$

$Q \rightarrow C$

the potential energy diagram looks like



What is E_a for the reaction $Q \rightarrow C$?

A-115 $E_a = 24 - 21 = 3$ kcal/mole

Q-116 In the reaction represented in Q-115, which step in the reaction would be the faster, $A + B \rightarrow Q$ or $Q \rightarrow C$?

A-116 $Q \rightarrow C$ would be the faster since the activation energy is less for this step.

Q-117 Sometimes the mechanism of a reaction can be changed by introduction of a catalyst A catalyst is a material which increases the rate of a chemical reaction without itself being used up. If a catalyst increases the rate of a chemical reaction, what happens to the activation energy?

A-117 Decreases; a change in rate is analogous to saying there is a change in E_a.

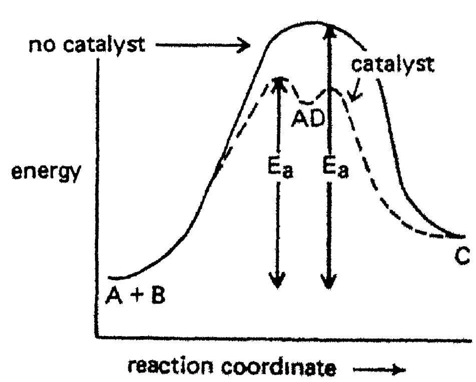
Q-118 The reaction $A + B \rightarrow C$ is very slow By use of a catalyst (D) the production of C can be greatly accelerated. The reaction mechanism now involves two steps:

$A + D \rightarrow AD$

$B + AD \rightarrow C + D$.

Draw a potential energy diagram to illustrate this reaction with and without a catalyst.

A-118



The activation energy for the catalyzed reaction is lower.

Q-119 Given the following two mechanisms, one with a catalyst, the other without:

1) $A + B \rightarrow C$ slow
   $C + B \rightarrow F + A$ fast

2) $B + B \rightarrow F$ slow .

Which mechanism uses the catalyst and what is it?

A-119 1) uses the catalyst and it is A

Overall reaction

$$A + 2B \rightarrow F + A$$

Q-120 For the chemical reaction

$$A + B \rightarrow C \quad \text{slow}$$
$$A + B \xrightarrow[(D)]{} C \quad \text{fast}$$

(the second reaction being the catalyzed reaction), propose a mechanism using catalyst D

A-120 1) $A + D \rightarrow F$
$F + B \rightarrow C + D$

or

2) $B + D \rightarrow G$
$G + A \rightarrow C + D$

Q-121 The mechanism for the overall reaction

$$A_2 + B \rightarrow D$$

is

$$A_2 \rightarrow 2A \quad \text{slow}$$
$$2A + B \rightarrow C \quad \text{fast} .$$

If a catalyst D changes the mechanism to

$$A_2 + D \rightarrow A_2D \quad \text{slow}$$
$$A_2D \rightarrow 2A + D \quad \text{fast}$$
$$2A + B \rightarrow C ,$$

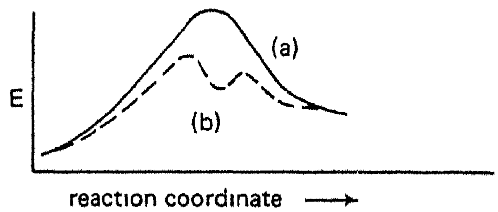
what is the rate expression for the reaction with and without a catalyst?

A-121 without rate $= k[A_2]$
with. rate $= k'[A_2]\,[D]$

Q-122 When using a catalyst, why does the energy of the activated complex change?

A-122 A new mechanism takes place which gives rise to a different activated complex

Q-123 Below is an energy diagram for a reaction with and without a catalyst·



Which path is used when the catalyst is used? Why will the reaction occur by this path?

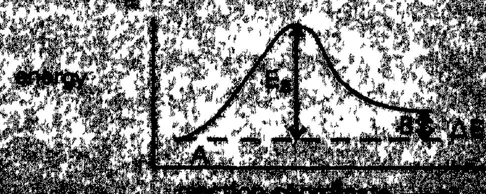
A-123 Path (b), a reaction will go by the path of least resistance, that is, the one with lowest activation energy

R a) $\ln(k) = \ln(A) - E_a/RT$

b) activation energy can be determined from a knowledge of the rate constant at two different temperatures.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\,\frac{(T_2 - T_1)}{T_1T_2}$$

c) potential energy diagram for the reaction $A_2 \rightarrow B$



d) a catalyst will change the [illegible] of a reaction; this will increase [illegible] rate of the reaction by producing a new mechanism in which all activat[illegible] complexes are lower than in the un[illegible]

PART III: Introduction to Equilibrium

S-1 The previous two parts introduced the factors which determine whether a chemical reaction will occur, how the reactants combine to form products, and the rate at which the reaction will take place In this part, concepts will be developed which will allow the determination of the extent to which a reaction will take place

Consider the reaction $A + B \rightleftharpoons C + D$ The double arrows indicate that while A and B react to form C and D, C and D also react to form A and B This is called a reversible reaction

Q-1 In a reversible reaction such as

$$A \rightleftharpoons B,$$

A can react to form B and B can react to form A Given that the forward reaction is first order with respect to A and the reverse reaction is first order with respect to B, write the rate expression for the forward and reverse reactions.

A-1 forward $rate_{(f)} = k_f[A]$

reverse $rate_{(r)} = k_r[B]$

(k_f and k_r are rarely the same)

Q-2 The following reaction takes place by a one step process in each direction·

$$2A \rightleftharpoons C + D.$$

Give the rate expressions for the forward and reverse reactions.

A-2 forward $rate_{(f)} = k_f[A]^2$

reverse $rate_{(r)} = k_r[C][D]$

Q-3 The reaction $A \rightleftharpoons B$ is allowed to proceed for a long period of time. On periodic analysis of the mixture, it is found that the reaction finally reaches a point where the concentration of A and B do not change. This reaction is said to have reached equilibrium. What can be said about the rates of the forward and reverse reactions at this time?

A-3 The forward rate must equal the reverse rate. $rate_{(f)} = rate_{(r)}$.

Q-4 Using the rate expression for the reversible reaction $A \rightleftharpoons B$ as

$$rate_{(f)} = k_f[A]$$

$$rate_{(r)} = k_r[B],$$

express the ratio k_f/k_r in terms of concentration of the reactant and product at equilibrium.

A-4

$$rate_{(f)} = rate_{(r)}$$

$$k_f[A] = k_r[B]$$

$$\frac{k_f}{k_r} = \frac{[B]}{[A]}$$

Q-5 Since the ratio of k_f/k_r is always a constant, what can be said about the ratio of concentration of B to A when equilibrium is obtained?

A-5 [B]/[A] is always the same and equals a constant, K, called the equilibrium constant

Q-6 Will the ratio [B]/[A] remain constant with temperature changes? Why?

A-6 No, the rate constants for the forward and reverse reactions change with temperature and not always to the same extent

Q-7 Write the rate expression for the forward and reverse reaction for the decomposition of hydrogen iodide,

$$2HI \rightleftharpoons H_2 + I_2 \ ,$$

assuming that the order of each component is the same as its molecularity

A-7 forward $\text{rate}_{(f)} = k_f[HI]^2$

reverse $\text{rate}_{(r)} = k_r[H_2][I_2]$

Q-8 Derive an expression for the equilibrium constant in terms of the forward and reverse rate constants for the reaction

$$2HI \rightleftharpoons H_2 + I_2 \ .$$

A-8 At equilibrium, $\text{rate}_{(f)} = \text{rate}_{(r)}$

$$k_f\,[HI]^2 = k_r[H_2]\,[I_2]$$

$$\frac{[H_2]\,[I_2]}{[HI]^2} = \frac{k_f}{k_r} = K_{eq.}$$

Q-9 In view of the answers for Q-5 and Q-8, define the equilibrium constant for the reaction

reactants $\rightleftharpoons$ products

in terms of the concentration of reactants and products

A-9

$$K_{eq.} = \frac{[\text{product}_1]\,[\text{product}_2]\ \ldots\text{etc}}{[\text{reactant}_1]\,[\text{reactant}_2]\ \ldots\text{etc}}$$

Q-10 Write the equilibrium constant for the reaction

$$2A + 3B \rightleftharpoons 4C + 2D \ .$$

A-10

$$K_{eq.} = \frac{[C]^4\,[D]^2}{[A]^2\,[B]^3}$$

S-2 LeChatelier's rule states that when stress is put on an equilibrated system, the system will re-equilibrate in an effort to minimize that stress. Common stresses which can be put on a chemical reaction are variations in concentration, pressure, or temperature.

Q-11 Consider the reaction $A + B \rightleftharpoons C + D$. If equilibrium has been reached and then some C is added to the system, which way will the reaction shift?

A-11 By adding C to the system, the rate of the reverse reaction increases over the rate of the forward reaction. Therefore, the reaction is said to have shifted to the left (A and B produced and D used up.)

Q-12 Consider the reaction $A + B \rightleftharpoons C + D$. If more B is added to an equilibrated system, which way would the reaction shift?

A-12 Adding $\underline{B}$ would increase the rate of the forward reaction Thus, more $\underline{C}$ and $\underline{D}$ would be produced and the reaction would shift to the right

Q-13 Consider the reaction $A + B \rightleftharpoons C$ in which reactants and products are gaseous The pressure on the system is increased, e g , by reducing the volume of the system How can the system minimize this stress?

A-13 The molar volume of all gases is essentially the same (1 mole of gas = 22 4 ℓ at STP) Since two moles of reactants combine to form only one mole of product, the increase in pressure can be minimized by forming more $\underline{C}$ Thus, the reaction will shift to the right

Q-14 Consider the gaseous equilibrium $A + B \rightleftharpoons C + D$ Which way will the reaction shift if pressure is decreased?

A-14 The reaction will remain essentially the same because two moles of reactants produce two moles of product and the total molar volume on both sides of the equation is the same

Q-15 Consider the gaseous equilibrium $A + B \rightleftharpoons 2C + D$. Which way will the reaction shift if the pressure on the system is decreased?

A-15 The reaction will shift to the right, i e , more product ($\underline{C}, \underline{D}$) will be formed The total molar volumes of reactants is less than the total molar volume of products Therefore, as total pressure is decreased, the reaction will equilibrate in such a way as to <u>increase</u> volume

Q-16 Consider the following system in equilibrium, $A + B \rightleftharpoons C + D$, in which ΔH is negative, i.e., an <u>exothermic</u> reaction (gives off heat). If heat is added to this system, which direction will the reaction shift?

A-16 By adding heat, a product is added to the right hand side of the equation, causing the rate of the reverse reaction to increase over the rate of the forward reaction More reactants ($\underline{A}, \underline{B}$) will be formed and the reaction will shift to the left.

Q-17 Consider the reaction $E + F \rightleftharpoons G$, in which ΔH is positive. If this <u>endothermic</u> reaction (<u>reaction which takes up heat</u>) is allowed to come to equilibrium at 25° and is then heated to 30°, which way will the reaction shift?

A-17 In this reaction, heat is a reactant (the reaction needs heat to take place). By adding more heat, a reactant is being added; therefore, more product will be produced and the reaction will be shifted to the right.

Q-18 For the reaction $A + B \rightleftharpoons C + D$, the equilibrium constant is 1. What can you say about the numerator and denominator of the equilibrium expression?

A-18

$$K_{eq} = \frac{[C]\,[D]}{[A]\,[B]} = 1$$

Therefore, $[C]\,[D] = [A]\,[B]$

Q-19 If the K_{eq} in the preceding problem had been 10^{-2}, which term would be larger, $[C]\,[D]$, or $[A]\,[B]$?

A-19 $$K_{eq} = \frac{[C]\,[D]}{[A]\,[B]} = 10^{-2}$$

Therefore, [A] [B] must be 100 times larger than [C] [D]

Q-20 Consider the two reactions

$$A + B \rightleftharpoons C \qquad K_{eq} = 1 \times 10^{-2}$$
$$E + F \rightleftharpoons G \qquad K_{eq} = 1 \times 10^{-4}$$

Which reaction goes further to completion, i e , converts the larger percent of starting material to product?

A-20 The ratio $\frac{[C]}{[A]\,[B]}$ is much larger than the ratio $\frac{[G]}{[E]\,[F]}$ Therefore, $A + B \rightleftharpoons C$ goes further toward completion.

Q-21 For the reaction $N + M \rightleftharpoons O + P$, the equilibrium constant is 10^{-14} Would you expect much O to be formed when mixing N and M? Why?

A-21 No, the ratio $\frac{[O]\,[P]}{[N]\,[M]}$ is 10^{-14}, therefore, very little N and M would be converted to O

Q-22 Consider the reaction $A + B \rightleftharpoons C + D$ If, at equilibrium, the concentration of A = 0 5, B = 0 7, C = 0.9, and D = 1.1 (all concentrations in mole per liter), what is the value of the equilibrium constant? What units will the equilibrium constant have?

A-22 $$K_{eq} = \frac{[C]\,[D]}{[A]\,[B]} = \frac{(0.9)\,(1\ 1)}{(0.5)\,(0\ 7)} = 2.8$$ (no units)

Q-23 Consider the reaction $A + B \rightleftharpoons C$ At equilibrium $[A] = 1.6 \times 10^{-2}$, $[B] = 5.2 \times 10^{-4}$, and $[C] = 6.0 \times 10^{-8}$ ([ ] means mole per liter) What is the value of K_{eq}? What units will the constant have?

A-23 $$K_{eq} = \frac{[C]}{[A]\,[B]} = \frac{6.0 \times 10^{-8}\ \text{mole}/\ell}{(1.6 \times 10^{-2})\,(5.2 \times 10^{-4})\ \text{mole}^2/\ell^2}$$
$$= 0.72 \times 10^{-2}\ \ell/\text{mole}$$

Q-24 Consider the reaction $2A \rightleftharpoons C + D$. At equilibrium $[A] = 9\ 2 \times 10^{-10}$, $[C] = 2\ 1 \times 10^{-4}$, and $[D] = 3\ 1 \times 10^{-4}$. What is the value of K_{eq}?

A-24 $$K_{eq} = \frac{[C]\,[D]}{[A]^2} = \frac{(2.1 \times 10^{-4})\,(3\ 1 \times 10^{-4})\ \text{mole}^2/\ell^2}{(9.2 \times 10^{-10})^2\text{mole}^2/\ell^2}$$
$$= 7.6 \times 10^{10}$$

Q-25 For the reaction $A + B \rightleftharpoons C + D$, the equilibrium constant is $1\ 0 \times 10^{-5}$. If the concentrations at equilibrium are [A] = 1.0, [B] = 2.0, and [C] = 3.0, what must the concentration of D be?

A-25 $$K_{eq} = \frac{[C]\,[D]}{[A]\,[B]} = 1.0 \times 10^{-5} = \frac{(3.0)\,[D]}{(1.0)(2.0)}$$

Therefore, $$[D] = \frac{(1.0 \times 10^{-5})(1.0)(2.0)}{(3.0)}$$
$$= 6.7 \times 10^{-6}\ \text{mole}/\ell$$

[redacted]

S-3 The equilibrium constant gives the extent to which a reaction takes place The change in free energy, ΔG°, also gives the extent to which a reaction goes to completion The larger the negative value for free energy, the greater will be the degree to which the reaction takes place Since ΔG° and K are both related to extent of reaction, they should be related to one another The relationship is expressed as

$$\Delta G^\circ = -RT(2\ 3) \log K_{eq}$$

where R is the gas constant in calories/deg (1 99), and T is the absolute temperature

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Q-26 For the decomposition of gaseous hydrogen peroxide according to the reaction

$$H_2O_{2(g)} \rightarrow H_2O_{(g)} + \tfrac{1}{2}O_{2(g)} ,$$

$\Delta G^\circ = -29.9$ kcal What is the value of the equilibrium constant for this reaction at 298° K?

A-26 $\Delta G^\circ = -RT\,(2\ 3) \log K_{eq}$

$$\log K_{eq} = \frac{(29\ 9 \text{ kcal})(1000 \text{ cal/kcal})}{(1\ 99 \text{ cal/deg})(2.3)(298^\circ)}$$

$$K_{eq} = 7\ 9 \times 10^{21}$$

Thus, a negative ΔG° corresponds to a large equilibrium constant

Q-27 When gaseous ozone, O_3, is formed from molecular oxygen by the reaction

$$\tfrac{3}{2}O_{2(g)} \rightarrow O_{3(g)} ,$$

the standard free energy change is +39.1 kcal. What is the equilibrium constant of this reaction at 298 K?

A-27 $\Delta G^\circ = -(2\ 3)RT \log K_{eq}$

$$\log K_{eq} = \frac{-(39\ 1 \text{ kcal})(1000 \text{ cal/kcal})}{(1\ 99 \text{ cal/deg})(2\ 3)(298^\circ)}$$

$$= -28\ 67$$

$$K_{eq} = 2\ 0 \times 10^{-29}$$

Thus, a large positive standard free energy change corresponds to a small equilibrium constant This indicates that the reaction is spontaneous in the reverse direction

Q-28 The equilibrium constant for the reaction

$$A + B \rightarrow C + D$$

at 25°C is 2.0×10^{10}. What is the standard free energy change for this reaction?

A-28 $\Delta G^\circ = -(2\ 3)RT \log K_{eq}$

$$\Delta G^\circ = -(2\ 3)(2\ 0 \text{ cal/deg})(298^\circ)\log 2\ 0 \times 10^{10}$$

$$\Delta G^\circ = -(2\ 3)(2\ 0)(298)(10\ 3)$$

$$\Delta G^\circ = -14{,}000 \text{ cal}$$

$$\Delta G^\circ = \frac{-14{,}000\ \cancel{\text{cal}}}{} \left| \frac{\text{kcal}}{1000\ \cancel{\text{cal}}} \right.$$

$$= 14 \text{ kcal}$$

Q-29 For the reaction

$$A + B \rightarrow C + D ,$$

the equilibrium concentration of each component is as follows:

A = 2.0 mole/ℓ

B = 4.0 mole/ℓ

C = 8.0 mole/ℓ

D = 7.0 mole/ℓ

What is the standard free energy value for this reaction at 25°C?

A-29 $K_{eq} = \dfrac{[C][D]}{[A][B]} = \dfrac{(8.0)(7.0)}{(4.0)(2.0)} = 7.0$

$\Delta G^\circ = -(2.3)RT \log K_{eq}$

$\Delta G^\circ = -(2.3)(2.0 \text{ cal/deg})(298^\circ)\log 7.0$

$\Delta G^\circ = \dfrac{-(2.3)(2.0)(298)(0.845)}{1000}$

$\Delta G^\circ = -1.16$ kcal

Q-30 Derive a relationship between equilibrium constant and standard enthalpy and entropy changes.
(Remember? $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$)

A-30 $\Delta G^\circ = -RT(2.3)\log K_{eq}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

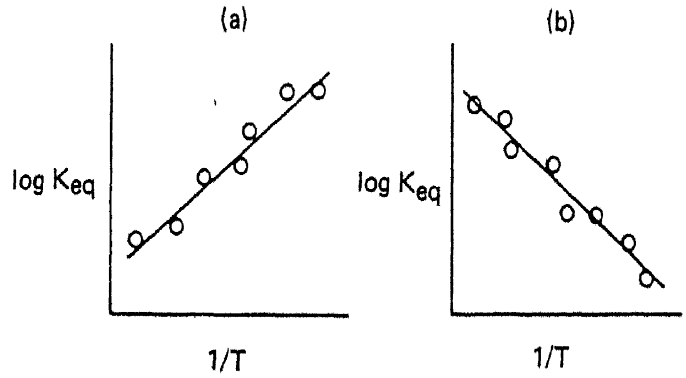
Set ΔG°'s equal to each other

$-RT(2.3)\log K_{eq} = \Delta H^\circ - T\Delta S^\circ$

Rearrange to give

$$\log K_{eq} = -\frac{\Delta H^\circ}{RT(2.3)} + \frac{\Delta S^\circ}{R(2.3)}$$

Q-31 By determining the equilibrium constant at various temperatures and plotting on a graph, ΔH° and ΔS° may be found. Plots of $\log K_{eq}$ vs $\frac{1}{T}$ are given



What is the slope equal to in the graph of $\log K_{eq}$ vs. $\frac{1}{T}$?

A-31 From the equation of a straight line

$y = ax + b$

a is the slope.

This can be compared with the equation

$$\log K_{eq} = -\frac{\Delta H^\circ}{RT(2.3)} + \frac{\Delta S^\circ}{R(2.3)}$$

Slope is equal to $\dfrac{-\Delta H^\circ}{R(2.3)}$.

Therefore, ΔH° can be found from the slope.

Q-32 What is the y intercept equal to in the graph of $\log K_{eq}$ vs. $\frac{1}{T}$?

A-32 y intercept is equal to $\dfrac{\Delta S^\circ}{R(2.3)}$

This is the usual way for determining the thermodynamic functions experimentally.

Q-33 What determines whether the graph in Q-31 is drawn as (a) or (b)?

A-33 (a) if ΔH° is negative

(b) if ΔH° is positive

Q-34 If two values of log K_{eq} are known at two different temperatures,

$\log K_{eq(1)}$ at $\frac{1}{T_1}$

$\log K_{eq(2)}$ at $\frac{1}{T_2}$,

derive an expression for determining ΔH° from this information

(Hint slope = $\frac{(y_2 - y_1)}{(x_2 - x_1)}$)

A-34

$$\text{slope} = \frac{\log K_{eq(2)} - \log K_{eq(1)}}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$\text{slope} = \frac{-\Delta H^\circ}{R(2\ 3)}$$

Set equal

$$\frac{\log \frac{K_{eq(2)}}{K_{eq(1)}}}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-\Delta H^\circ}{R(2\ 3)}$$

Rearrange to give

$$\log \frac{K_{eq(2)}}{K_{eq(1)}} = \frac{-\Delta H}{R(2\ 3)} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Q-35 At 298° K, the equilibrium constant and ΔH° for the reaction

$$2NO_{2(g)} \rightarrow N_2O_{4(g)}$$

are 8 8 and -13 9 kcal, respectively What is the value of the equilibrium constant at 273° K?

(Hint Use equation derived in A-34)

A-35

$$\log \frac{K_{eq(2)}}{K_{eq(1)}} = \frac{-\Delta H^\circ}{R(2\ 3)} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{K_{eq(2)}}{8\ 8} = \frac{-(-13{,}900)}{(2\ 0)(2.3)} \left(\frac{1}{273} - \frac{1}{298} \right)$$

$$K_{eq(2)} = 7\ 1$$

Q-36 The equilibrium constant for the reaction

$$2HI_{(g)} = H_{2(g)} + I_{2(g)}$$

is 2.18×10^{-2} at 764° K, and is 1.64×10^{-2} at 667° K. Find ΔH° for the reaction.

A-36

$$\log \frac{K_{eq(2)}}{K_{eq(1)}} = \frac{-\Delta H^\circ}{R(2\ 3)} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{2\ 18 \times 10^{-2}}{1.64 \times 10^{-2}} = \frac{-\Delta H^\circ}{(2.0)(2.3)} \left(\frac{1}{764} - \frac{1}{667} \right)$$

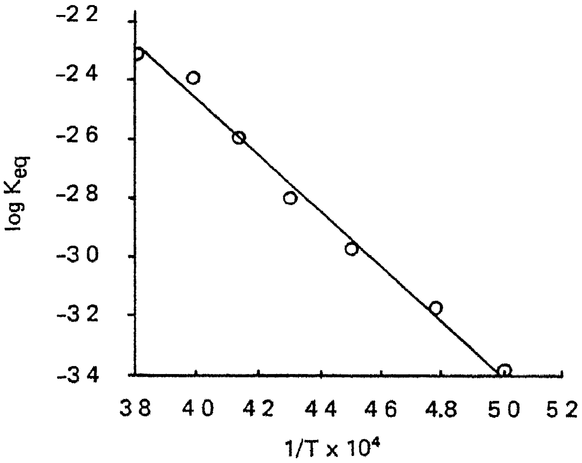
ΔH = 3000 cal

Q-37 Prepare a plot of the following experimental data for the reaction

$$N_2 + O_2 \rightleftharpoons 2NO$$

$\log K_{eq}$	$\frac{1}{T}$ deg^{-1}
-2.3	3.80×10^{-4}
-2.4	4.00×10^{-4}
-2.6	4.15×10^{-4}
-2.8	4.30×10^{-4}
-3.0	4.55×10^{-4}
-3 2	4.80×10^{-4}
-3.4	5.00×10^{-4}

A-37



Q-38 Find ΔH° for the reaction by using a graphical procedure

A-38

$$\text{slope} = \frac{-\Delta H^\circ}{R(2\ 3)}$$

$$-0\ 94 \times 10^4 = \frac{-\Delta H^\circ}{(2\ 0)(2\ 3)}$$

$$\Delta H^\circ = 4\ 32 \times 10^4 \text{ cal}$$

[redacted]

TABLE I

STANDARD HEATS OF FORMATION, ΔH_f°

Compound	ΔH_f° (kcal/mole)	Compound	ΔH_f° (kcal/mole)	Compound	ΔH_f° (kcal/mole)
$Al(s)$	0.00	$C_5H_{12}(g)$	-35.00	$H_2O_2(\ell)$	-44.88
$Al_2O_3(s)$	-399.09	$C_5H_{12}(\ell)$	-41.36	$I_2(g)$	14.88
$Br_2(g)$	7.34	$C_6H_6(g)$	19.82	$I_2(s)$	0.00
$Br_2(\ell)$	0.00	$C_6H_6(\ell)$	11.72	$N_2(g)$	0.00
$Ca(s)$	0.00	$C_6H_{12}(\ell)$	-9.96	$NH_3(g)$	-11.04
$C(g)$	171.70	$C_6H_{14}(g)$	-39.96	$N_2O(g)$	19.49
C(graphite)	0.00	$C_6H_{14}(\ell)$	-47.52	$NO(g)$	21.60
$CaCO_3(s)$	-288.45	$CH_3OH(g)$	-48.08	$NO_2(g)$	8.09
$CaO(s)$	-151.9	$C_2H_5OH(g)$	-56.63	$N_2O_4(g)$	2.31
$Cl_2(g)$	0.00	$CO(g)$	-26.42	$O_2(g)$	0.00
$CH_4(g)$	-17.89	$CO_2(g)$	-94.05	$O_3(g)$	34.0
$C_2H_2(g)$	54.19	$H_2(g)$	0.00	$S(s)$	0.00
$C_2H_4(g)$	12.50	$HBr(g)$	-8.66	$Si(s)$	0.00
$C_2H_6(g)$	-20.24	$HCl(g)$	-22.06	$SiO_2(s)$	-205.4
$C_3H_6(g)$	4.88	$HI(g)$	6.20	$SO_2(g)$	-70.96
$C_3H_8(g)$	-24.82	$H_2O(g)$	-57.80	$SO_3(g)$	-94.45
$C_4H_{10}(g)$	-29.81	$H_2O(\ell)$	-68.32		

From Selected Values of Chemical Thermodynamic Properties, ed F A Rossini, et. al., National Bureau of Standards Circular 500

TABLE II

STANDARD ENTROPIES, S°

Compound	S° (cal/mole-deg)	Compound	S° (cal/mole-deg)	Compound	S° (cal/mole-deg)
$Al(s)$	6.77	$C_5H_{12}(g)$	83.27	$I_2(g)$	62.28
$Al_2O_3(s)$	12.19	$C_5H_{12}(\ell)$	62.79	$I_2(s)$	27.9
$Br_2(g)$	58.64	$C_6H_6(g)$	64.34	$N_2(g)$	45.77
$Br_2(\ell)$	36.4	$C_6H_6(\ell)$	41.30	$NH_3(g)$	46.01
$Ca(s)$	9.95	$C_6H_{12}(\ell)$	92.25	$N_2O(g)$	52.58
$C(g)$	37.76	$C_6H_{14}(g)$	92.45	$NO(g)$	50.34
C(graphite)	1.37	$C_6H_{14}(\ell)$	70.34	$NO_2(g)$	57.47
$CaCO_3(s)$	22.2	$CH_3OH(g)$	56.8	$N_2O_4(g)$	72.73
$CaO(s)$	9.5	$C_2H_5OH(g)$	67.4	$O_2(g)$	49.00
$Cl_2(g)$	53.29	$CO(g)$	47.30	$O_3(g)$	56.8
$CH_4(g)$	44.50	$CO_2(g)$	51.06	$S(s)$	7.62
$C_2H_2(g)$	48.00	$H_2(g)$	31.21	$Si(s)$	4.47
$C_2H_4(g)$	52.45	$HBr(g)$	47.44	$SiO_2(s)$	10.00
$C_2H_6(g)$	54.85	$HCl(g)$	44.62	$SO_2(g)$	59.40
$C_3H_6(g)$	63.80	$HI(g)$	49.31	$SO_3(g)$	61.24
$C_3H_8(g)$	64.51	$H_2O(g)$	45.11		
$C_4H_{10}(g)$	74.10	$H_2O(\ell)$	16.72		

From Selected Values of Chemical Thermodynamic Properties, ed. F. A. Rossini, et. al, National Bureau of Standards Circular 500.

TABLE III

STANDARD FREE ENERGY OF FORMATION, ΔG_f°

Compound	ΔG_f° (kcal/mole)	Compound	ΔG_f° (kcal/mole)	Compound	ΔG_f° (kcal/mole)
$Al(s)$	0 00	$C_5H_{12}(g)$	-1 96	$I_2(g)$	4 63
$Al_2O_3(s)$	-376.77	$C_5H_{12}(\ell)$	-2 21	$I_2(s)$	0.00
$Br_2(g)$	0 751	$C_6H_6(g)$	30 99	$N_2(g)$	0 00
$Br_2(\ell)$	0 00	$C_6H_6(\ell)$	29 76	$NH_3(g)$	-3 98
$Ca(s)$	0 00	$C_6H_{12}(\ell)$	20 80	$N_2O(g)$	24 76
$C(g)$	160 84	$C_6H_{14}(g)$	0 05	$NO(g)$	20 72
C(graphite)	0 00	$C_6H_{14}(\ell)$	20 80	$NO_2(g)$	12 39
$CaCO_3(s)$	-269.78	$CH_3OH(g)$	-38 69	$N_2O_4(g)$	23 49
$CaO(s)$	-144.4	$C_2H_5OH(g)$	-40 69	$O_2(g)$	0 00
$Cl_2(g)$	0 00	$CO(g)$	-32 81	$O_3(g)$	39.0
$CH_4(g)$	-12 14	$CO_2(g)$	-94 26	$S(s)$	0.00
$C_2H_2(g)$	50 00	$H_2(g)$	0 00	$Si(s)$	0.00
$C_2H_4(g)$	16 28	$HBr(g)$	-12 72	$SiO_2(s)$	-192.4
$C_2H_6(g)$	-7 86	$HCl(g)$	-22 77	$SO_2(g)$	-71 79
$C_3H_6(g)$	14 99	$HI(g)$	0 31	$SO_3(g)$	-88 52
$C_3H_8(g)$	-5.61	$H_2O(g)$	-54 64		
$C_4H_{10}(g)$	-3 75	$H_2O(\ell)$	-56 69		

From Selected Values of Chemical Thermodynamic Properties, ed F A Rossini, et al, National Bureau of Standards Circular 500

TABLE IV

BOND ENERGIES

Bond	Bond energy (kcal/mole)	Bond	Bond energy (kcal/mole)	Bond	Bond energy (kcal/mole)
Br—Br	46	C=O	173	N—H	92
C—C	80	C≡O	256	N—N	37
C=C	145	Cl—Cl	57	N≡N	225
C≡C	194	F—F	38	N=O	150
C—Cl	78	H—Br	88	O—H	109
C—F	116	H—Cl	103	O—O	33
C—H	99	H—F	135	O=O	117
C—N	70	H—H	103	S—H	85
C≡N	212	H—I	71		
C—O	82	I—I	36		

From Selected Values of Chemical Thermodynamic Properties, ed. F. A Rossini, et al, National Bureau of Standards Circular 500

NOTES

Chapter 8 CHEMICAL EQUILIBRIUM

Part I Homogeneous and Heterogeneous Equilibrium

After completing this section you should be able to

a) understand the qualitative effects of Le Chatelier's rule
b) calculate the quantitative effect on an equilibrated system of changing pressure or concentration
c) understand the difference between homogeneous and heterogeneous equilibrium

Part II Application of Equilibrium Theory

After completing this section you should be able to

a) understand the difference between strong and weak acids and bases in terms of equilibrium constants
b) understand soluble and insoluble salts in terms of equilibrium constants
c) calculate the quantitative effect on an equilibrated system caused by adding a common ion or complexing ion.

Part III. Acid-Base Titrations

After completing this section you should be able to

a) compute the pH at the equivalence point for the titration of a weak acid with a strong base and vice versa
b) understand how indicators are used
c) determine which indicator should be used for a particular titration

Part IV· Complex Ions

After completing this section you should be able to

a) calculate the equilibrium concentrations of a complex metal ion in a solution containing metal ions and complexing ligands
b) calculate the concentration of complexing ligand required to dissolve a quantity of insoluble salt
c) calculate the concentration of complexing ligand required to prevent the precipitation of an insoluble salt

PART I: Homogeneous and Heterogeneous Equilibrium

S-1 When a system is at equilibrium no overall change is observed. However, a reversible reaction is occurring with the rate of the forward reaction equal to the rate of the reverse reaction. Consider the reaction

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d}$$

The double arrows indicate that while $\underline{a}$ and $\underline{b}$ react to form $\underline{c}$ and $\underline{d}$, $\underline{c}$ and $\underline{d}$ also react to form $\underline{a}$ and $\underline{b}$. This is called a reversible reaction. The rate at which $\underline{a}$ and $\underline{b}$ react to form $\underline{c}$ and $\underline{d}$ will

1) increase with increasing concentration of $\underline{a}$ and/or $\underline{b}$ (in fact, the rate is directly proportional to the product of the concentration of the reactants),
2) increase with increasing temperature (many reaction rates will approximately double for every 10° increase in temperature).

For the reaction given above,

$$\text{Rate}_{\text{forward reaction}} = k_f[\underline{a}][\underline{b}]$$
$$\text{Rate}_{\text{reverse reaction}} = k_r[\underline{c}][\underline{d}]$$

where k_f and k_r are proportionality constants called rate constants. The brackets around $\underline{a}$, $\underline{b}$, $\underline{c}$ and $\underline{d}$ indicate that the concentrations of these species are given in moles/liter.

Q-1 If a system is at equilibrium, will the rate of the forward reaction be less than, equal to, or greater than the rate of the reverse reaction?

A-1 Equal to

Q-2 Periodic analysis of a mixture at equilibrium shows that the concentrations of reactants and products remain unchanged. Does this indicate that the chemical reaction has ceased? Explain.

A-2 No. The chemical reaction continues, but the rate at which product is formed is just equal to the rate at which product decomposes to reactant.

Q-3 The equilibrium constant for a reaction is defined as the ratio of k_f to k_r. Derive the equilibrium expression for the reaction

$$2\underline{a} \rightleftharpoons \underline{c} + \underline{d}\,.$$

(Hint: $\text{Rate}_{\text{forward}} = k_f[\underline{a}]^2$, $\underline{c}$ and $\underline{d}$ are first order for the reverse reaction.)

A-3 At equilibrium

$$\text{rate}_f = \text{rate}_r$$

Therefore,

$$k_f[\underline{a}]^2 = k_r[\underline{c}][\underline{d}]$$

$$\frac{k_f}{k_r} = \frac{[\underline{c}][\underline{d}]}{[\underline{a}]^2} = K_{eq}$$

Q-4 Equilibrium constants vary with temperature. Explain why a temperature change should affect equilibrium.

A-4 Increasing the temperature will change the rate constant of both the forward and reverse reaction It is unlikely that the effect on rate constants will be exactly the same, therefore, K_{eq} will change with temperature

Q-5 The substances $\underline{a}$, $\underline{b}$ and $\underline{c}$ are at equilibrium according to the equation

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c}$$

A quantity of c is added to the system After equilibrium is reached again, will the value of K_{eq} be different? Why?

(Hint Are rate constants affected by concentrations?)

A-5 No K_{eq} is dependent upon k_f and k_r The rate constants are not affected by concentrations

R An equilibrium constant is defined as the ratio of k_f/k_r.

$$K_{eq} = \frac{[\text{Product}_1][\text{Product}_2]}{[\text{Reactant}_1][\text{Reactant}_2]}$$

S-2 Le Chatelier's rule states that when a stress is put on an equilibrated system, the system will re-equilibrate to minimize that stress Common stresses which affect chemical reactions are variations in concentration, pressure or temperature. For example, in the gaseous reaction $\underline{a} + \underline{b} \rightleftharpoons \underline{c}$, two molecules combine to give one molecule Increasing the pressure of $\underline{a}$, $\underline{b}$ and $\underline{c}$ puts a stress on the system which can be relieved by reducing the number of gas molecules in the system The number of gas molecules is reduced by the conversion of $\underline{a}$ and $\underline{b}$ to $\underline{c}$.

The effect of changing the temperature of an equilibrated system can also be predicted In the reaction

$$\underline{e} \rightleftharpoons \underline{f} \qquad \Delta H = +30 \text{ kcal (endothermic)}$$

energy is absorbed when $\underline{e}$ is converted to $\underline{f}$ Increasing the temperature places a stress on the system which can be relieved by converting more $\underline{e}$ to $\underline{f}$ (absorbing energy)

Q-6 Consider the reaction

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d}$$

If equilibrium has been reached and then some $\underline{c}$ is added to the system, Le Chatelier's rule states that more $\underline{a}$ and $\underline{b}$ will be formed Will the addition of $\underline{c}$ affect the rate of the forward or the reverse reaction? How?

A-6 The rate of the reverse reaction is increased when $\underline{c}$ is added to the system. If $[\underline{c}]$ is increased, the rate must increase because of the relationship

$$\text{rate}_{\text{reverse}} = k[\underline{c}][\underline{d}] .$$

Q-7 Will the addition of $\underline{c}$ to the system

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d}$$

change K_{eq}?

Will the addition of $\underline{c}$ change $[\underline{c}][\underline{d}]/[\underline{a}][\underline{b}]$ at equilibrium?

A-7 K_{eq} does not change, and the ratio of $[\underline{c}][\underline{d}]$ to $[\underline{a}][\underline{b}]$ must be constant.

Q-8 For the system

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d} ,$$

how is it possible for the ratio $[\underline{c}][\underline{d}]/[\underline{a}][\underline{b}]$ to remain constant when more $\underline{c}$ is added?

A-8 Some of the $\underline{c}$ added reacts with $\underline{d}$ to increase the concentration of $\underline{a}$ and $\underline{b}$ until the ratio $[\underline{c}][\underline{d}]/[\underline{a}][\underline{b}]$ equals K_{eq}

Q-9 For gaseous reactions, concentrations are usually expressed in partial pressure Starting with the gas law $PV = nRT$, show that at constant temperature, pressure is directly related to concentration in moles/liter

A-9 $PV = nRT$

$P = \frac{n}{V} RT$

At constant temperature, RT is a constant. n/V is concentration expressed in moles per unit volume.

Q-10 For the gaseous reaction

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d}$$

write the equilibrium expression in terms of partial pressures

A-10 $$K_p = \frac{(P_{\underline{c}})(P_{\underline{d}})}{(P_{\underline{a}})(P_{\underline{b}})}$$

Q-11 For the reaction

$$\underline{a} + \underline{b} \rightarrow \underline{c}$$

write the expression for K_{eq} and K_p Give the units for K_{eq} (concentrations in mole/liter) and for K_p (pressure in atm)

A-11 $$K_{eq} = \frac{[\underline{c}] \quad \text{mole}/\ell}{[\underline{a}][\underline{b}] \ (\text{mole}/\ell)^2}$$

$$K_{eq} = \frac{[\underline{c}] \ \ell/\text{mole}}{[\underline{a}][\underline{b}]}$$

$$K_p = \frac{P_{\underline{c}} \ \text{atm}}{P_{\underline{a}} P_{\underline{b}} \ (\text{atm})^2}$$

$$K_p = \frac{P_{\underline{c}}}{P_{\underline{a}} P_{\underline{b}} \ \text{atm}}$$

Q-12 For the reaction

$$\underline{d} + \underline{f} \rightarrow \underline{g} + \underline{h}$$

what are the units for K_{eq} (concentrations given in mole/ℓ) and for K_p (pressure in atm)

A-12 K_{eq} is unitless

$$K_{eq} = \frac{[\underline{g}][\underline{h}] \ \cancel{(\text{mole}/\ell)^2}}{[\underline{d}][\underline{f}] \ \cancel{(\text{mole}/\ell)^2}}$$

K_p is unitless

$$K_p = \frac{P_{\underline{g}} P_{\underline{h}} \cancel{\text{atm}^2}}{P_{\underline{d}} P_{\underline{f}} \cancel{\text{atm}^2}}$$

Q-13 From the answer given in A-11, and the gas law, $PV = nRT$, derive the relationship between K_p and K_{eq} for the reaction

$$\underline{a} + \underline{b} \rightarrow \underline{c}$$

(Hint: For the gas $\underline{a}$,

$$\frac{n_{\underline{a}}}{V} = [\underline{a}] \ .)$$

A-13 $$K_p = \frac{P_{\underline{c}}}{P_{\underline{a}} P_{\underline{b}}}$$

$$\frac{n_{\underline{a}}}{V} = \frac{P_{\underline{a}}}{RT} \qquad \frac{n_{\underline{a}}}{V} = [\underline{a}]$$

Therefore,

$P_{\underline{c}} = RT[\underline{c}]$

$P_{\underline{a}} = RT[\underline{a}]$

$P_{\underline{b}} = RT[\underline{b}]$

$$K_p = \frac{[\underline{c}]RT}{[\underline{a}]RT[\underline{b}]RT} = \frac{[\underline{c}]}{[\underline{a}][\underline{b}]RT}$$

$K_p = K_{eq}/RT$

Q-14 For the reaction

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d}$$

the partial pressures at equilibrium are $P_{\underline{a}} = 0.40$ atm, $P_{\underline{b}} = 0.30$ atm, $P_{\underline{c}} = 0.20$ atm, $P_{\underline{d}} = 0.10$ atm. Calculate K_p.

A-14 $K_p = \frac{(P_c)(P_d)}{(P_a)(P_b)} = \frac{(0\ 20)(0\ 10)}{(0\ 40)(0\ 30)} = 0\ 17$

Q-15 Increasing the pressure of a gaseous reaction will not change K_{eq} or K_p For the reaction given in Q-14, the volume is reduced by one half Will the partial pressures of any reactants or products change? Will the ratio P_cP_d/P_aP_b change?

A-15 If the volume is reduced by one half, the partial pressure of each component is doubled

$P_a = 0\ 80$ atm, $P_b = 0\ 60$ atm,

$P_c = 0\ 40$ atm, and $P_d = 0\ 20$ atm

The ratio P_cP_d/P_aP_b remains at 0 17.

Q-16 For the gaseous reaction

$$e + f \rightleftharpoons g$$

the partial pressures at equilibrium are $P_e = 0\ 30$ atm, $P_f = 0.20$ atm and $P_g = 0\ 60$ atm

What is K_p for this reaction? According to Le Chatelier's rule, how will increasing the pressure on the system, by reducing the volume, affect the equilibrium?

A-16 $K_p = \frac{(P_g)}{(P_e)(P_f)} = \frac{(0\ 60)}{(0.30)(0\ 20)} = 10\ \text{atm}^{-1}$

According to Le Chatelier's rule, increasing pressure will shift the reaction to the right (produce more g)

Q-17 For the system described in Q-16, the volume was reduced When equilibrium was re-established, it was found that P_e and P_f were doubled. Show that, in accordance with Le Chatelier's rule, P_g was more than doubled

A-17 $K_p = \frac{(P_g)}{(P_e)(P_f)} = 10\ \text{atm}^{-1}$

$$\frac{(P_g)}{(P_e)(P_f)} = \frac{(P_g)}{(0.60)(0.40)} = 10\ \text{atm}^{-1}$$

$P_g = (10)(0.60)(0.40) = 2\ 4$ atm

2 times $P_{g(\text{initial})} = 1\ 2$ atm

Q-18 The reactants c and d are allowed to react in a vessel according to the equation

$$c_{(g)} + d_{(g)} \rightleftharpoons m_{(g)}\ .$$

After equilibrium is established, the partial pressures were $P_c = 0.20$ atm, $P_d = 0.40$ atm and $P_m = 2\ 0$ atm Calculate K_p for this reaction. According to LeChatelier's rule, how will increasing the volume of the reaction vessel affect this equilibrium?

A-18 For the reaction

$$K_p = \frac{(P_m)}{(P_c)(P_d)} = \frac{(2.0)}{(0.20)(0.40)} = 25\ \text{atm}^{-1}$$

According to Le Chatelier's rule, increasing the volume will shift the reaction to the left. The reaction which produces c and d is favored because it increases the number of molecules in the system.

Q-19 Consider the reaction

$$a + b \rightleftharpoons c$$

in which the reactants and products are gaseous. The pressure on the system is doubled by reducing the volume of the system. Le Chatelier's rule states that more c will be formed. Give a kinetic interpretation of this phenomenon.

A-19 $\text{rate}_{\text{forward}} = k_f[\underline{a}][\underline{b}]$

$\text{rate}_{\text{reverse}} = k_r[\underline{c}]$

If the volume is reduced so as to double the partial pressure of a, b and c, then [a], [b] and [c] will be doubled initially The rate of the forward reaction will quadruple while the rate of the reverse reaction will only double, thus, more c will form

Q-20 The gaseous system $\underline{a} + \underline{b} \rightleftharpoons \underline{c}$ is in equilibrium in a 1 liter vessel Pressure is increased by pumping in an inert gas, the volume remains constant Will the partial pressure of a, b and c change? Does the concentration of c change? (Hint Remember Dalton's Law)

A-20 Pumping in an inert gas will increase the total pressure, but will not change the partial pressure of a, b or c Therefore, the concentration of a, b or c will not change.

Q-21 The gaseous system

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c}$$

is in equilibrium in a 1 liter vessel An inert gas is pumped into the vessel and the vessel is allowed to expand so that the initial pressure of the system is maintained Does the expansion place a stress on the system? How can the stress be relieved?

A-21 Yes As the vessel expands, $P_{\underline{a}}$, $P_{\underline{b}}$ and $P_{\underline{c}}$ decrease In order for the ratio $P_{\underline{c}}/P_{\underline{a}}P_{\underline{b}}$ to remain constant, the partial pressure of c must decrease more than the partial pressures of a and b. Therefore, some c must decompose to form a and b.

Q-22 For the reaction

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d}$$

the change in enthalpy (ΔH) is -10 kcal. A negative enthalpy means that the forward reaction is exothermic (releases heat). If heat is added to the system, will more a and b form?

A-22 More a and b will form The rate constant for the reverse reaction is increased more than the rate constant for the forward reaction. This is the general case for an exothermic reaction.

Q-23 For the equilibrated system,

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d}$$

increasing the temperature will cause a change in the concentrations of reactants and products. Adding more a to the equilibrated system causes more c and d to be formed. Does K_{eq} change in either of these situations? Explain.

A-23 As temperature changes, the ratio k_f/k_r changes; therefore, K_{eq} changes as temperature changes When concentrations change, the rate constants k_f and k_r are unaffected; therefore, K_{eq} remains constant The rate of the forward and reverse reactions change with changing concentration but not the rate constants.

[redacted]

S-3 The value of an equilibrium constant must be determined from experimental data. In Chapter 7 it was shown how K_{eq} could be evaluated from thermodynamic data. The equilibrium constant can also be evaluated if the initial concentrations of reactants and products and the equilibrium concentration of one component are known. For the reaction

$$\underline{a} + \underline{b} \rightleftarrows \underline{c} + \underline{d}$$

the initial concentrations of $\underline{a}$ and $\underline{b}$ were 1.0 M and 2.0 M respectively. The initial concentration of $\underline{c}$ and $\underline{d}$ was zero. At equilibrium, the concentration of $\underline{c}$ was found to be 0.3 M. Therefore, at equilibrium

$$[\underline{a}] = 1.0\text{ M} - 0.3\text{ M} \qquad [\underline{b}] = 2.0\text{ M} - 0.3\text{ M}$$

$$[\underline{c}] = [\underline{d}] = 0.3\text{ M}$$

$$K_{eq} = \frac{(0.3)^2}{(0.7)(1.7)} = 0.08$$

Q-24 At room temperature, $\underline{a}$ and $\underline{b}$ react according to the equation

$$\underline{a} + \underline{b} \rightleftarrows \underline{c}$$

The initial concentrations of $\underline{a}$ and $\underline{b}$ were made 1.0 M ($[\underline{c}] = 0$). At equilibrium, the concentration of $\underline{c}$ was found to be 0.2 M. What is the equilibrium constant for this reaction?

A-24 At equilibrium

$$[\underline{c}] = 0.2\text{ M}$$

$$[\underline{a}] = [\underline{b}] = 1.0\text{ M} - 0.2\text{ M} = 0.8\text{ M}$$

$$K_{eq} = \frac{[\underline{c}]}{[\underline{a}][\underline{b}]} = \frac{(0.2)}{(0.8)(0.8)} = 0.3\ \ell/\text{mole}$$

Q-25 The substances $\underline{d}$ and $\underline{e}$ are mixed in solution and form $\underline{m}$ and $\underline{n}$ according to the equation

$$\underline{d} + \underline{e} \rightleftarrows \underline{m} + \underline{n}$$

The initial concentrations of $\underline{d}$ and $\underline{e}$ are 1.00 mole/liter. At equilibrium, the concentration of $\underline{m}$ is 0.90 mole/liter. What is K_{eq} for the reaction?

A-25 At equilibrium

$$[\underline{m}] = [\underline{n}] = 0.90\text{ M}$$

$$[\underline{d}] = [\underline{e}] = 1.00 - 0.90 = 0.10\text{ M}$$

$$K_{eq} = \frac{[\underline{m}][\underline{n}]}{[\underline{d}][\underline{e}]} = \frac{(0.90)(0.90)}{(0.10)(0.10)} = 81$$

Q-26 Reactants $\underline{q}$ and $\underline{r}$ form s according to the following equation

$$\underline{q} + \underline{r} \rightleftarrows \underline{s}$$

The initial concentrations of $\underline{q}$ and $\underline{r}$ were 0.8 and 1.5 mole/liter, respectively ($[\underline{s}] = 0$). At equilibrium the concentration of $\underline{s}$ was 0.3 mole/liter. What is the equilibrium constant for the reaction?

A-26 At equilibrium

$$[\underline{s}] = 0.3\text{ M}$$

$$[\underline{q}] = 0.8 - 0.3 = 0.5\text{ M}$$

$$[\underline{r}] = 1.5 - 0.3 = 1.2\text{ M}$$

$$K_{eq} = \frac{[\underline{s}]}{[\underline{q}][\underline{r}]} = \frac{(0.3)}{(0.5)(1.2)} = 0.5\ \ell/\text{mole}$$

Q-27 For the reaction

$$\underline{t} + \underline{v} \rightleftarrows 2\underline{u}$$

the initial concentration of $\underline{t}$ was 1.0 mole/liter and that of $\underline{v}$ was 2.0 mole/liter ($[\underline{u}] = 0$). At equilibrium the vessel contained 0.2 mole/liter of $\underline{u}$. What is K_{eq}?

A-27 At equilibrium

$[\underline{u}] = 0.2\ M$

$[\underline{t}] = 1.0 - 0.1 = 0.9\ M$ (for every two moles of $\underline{u}$ formed, 1 mole of $\underline{t}$ is consumed.)

$[\underline{v}] = 2.0 - 0.1 = 1.9\ M$

$$K_{eq} = \frac{[\underline{u}]^2}{[\underline{t}][\underline{v}]} = \frac{(0.2)^2}{(0.9)(1.9)} = 0.02$$

Q-28 For the reaction

$$\underline{d} + 2\underline{e} \rightleftharpoons \underline{f}$$

the initial concentrations of d and e were 0.2 mole/liter and 1.2 mole/liter, respectively ($[\underline{f}] = 0$). At equilibrium, the concentration of $\underline{f}$ was found to be 0.1 mole/liter. What is K_{eq} for this reaction?

A-28 At equilibrium

$[\underline{d}] = 0.2 - 0.1 = 0.1\ M$

$[\underline{e}] = 1.2 - 2(0.1) = 1.0\ M$

$[\underline{f}] = 0.1\ M$

$$K_{eq} = \frac{[\underline{f}]}{[\underline{d}][\underline{e}]^2} = \frac{(0.1)}{(0.1)(1.0)^2} = 1\ \ell^2/\text{mole}^2$$

Q-29 A compound, HB, is formed from H and B according to the equation

$$H + B \rightleftharpoons HB$$

A solution was prepared by dissolving 0.100 mole of H and 0.100 mole of B in enough water to make the total volume equal to one liter. After equilibrium had been established, it was found that 20% of H had reacted. What are the equilibrium concentrations of H, B and HB? What is K_{eq} for the reaction?

A-29 At equilibrium

$[HB] = (0.100)(0.20) = 0.020\ M$

$[H] = 0.100 - 0.020 = 0.080\ M$

$[B] = 0.100 - 0.020 = 0.080\ M$

$$K_{eq} = \frac{(0.020)}{(0.080)^2} = 3.1\ \ell/\text{mole}$$

[illegible]

S-4 If all the reactants and products of a reaction are in a single phase (i.e., all in the gas phase, or all in solution), then concentration factors for all the components appear in the equilibrium expression. If K_{eq} and all but one of the concentrations appearing in the equilibrium expression are known, then the unknown concentration may be calculated.

Q-30 For the reaction

$$\underline{a} + \underline{b} \rightleftharpoons \underline{c} + \underline{d},$$

the equilibrium constant is 1.0×10^{-5}. If the concentrations at equilibrium are $[\underline{a}] = 1.0\ M$, $[\underline{b}] = 2.0\ M$ and $[\underline{c}] = 3.0\ M$, what must the concentration of $\underline{d}$ be? Remember, brackets enclosing a reactant or product always indicate concentrations in mole/ℓ.

A-30

$$K_{eq} = \frac{[\underline{c}]\,[\underline{d}]}{[\underline{a}]\,[\underline{b}]} = \frac{[3.0]\,[\underline{d}]}{[1.0]\,[2.0]} = 1.0 \times 10^{-5}$$

Therefore,

$$[\underline{d}] = \frac{(1.0 \times 10^{-5})\,(1.0)\,(2.0)}{3.0}\ M$$

$$= 6.7 \times 10^{-6}\ M$$

Q-31 For the reaction

$$2\underline{a} \rightleftarrows \underline{c} + \underline{d},$$

the equilibrium constant is 1.0×10^{-3}. At equilibrium, the concentrations observed were

$$[\underline{c}] = 1.2 \times 10^{-3}\ M$$

$$[\underline{d}] = 3.8 \times 10^{-6}\ M$$

What was $[\underline{a}]$ at equilibrium?

A-31

$$K_{eq} = \frac{[\underline{c}]\,[\underline{d}]}{[\underline{a}]^2} = 1.0 \times 10^{-3}$$

$$\frac{[\underline{c}]\,[\underline{d}]}{[\underline{a}]^2} = \frac{(1.2 \times 10^{-3})\,(3.8 \times 10^{-6})}{[\underline{a}]^2} = 1.0 \times 10^{-3}$$

$$[\underline{a}]^2 = \frac{(1.2 \times 10^{-3})\,(3.8 \times 10^{-6})}{1.0 \times 10^{-3}}$$

$$= 4.6 \times 10^{-6}\ \text{mole}^2/\ell^2$$

Therefore,

$$[\underline{a}] = 2.1 \times 10^{-3}\ M$$

Q-32 For the reaction

$$\underline{a} \rightleftarrows \underline{b}$$

the equilibrium constant is 1.0×10^{-4} at 60°. A solution initially containing 1.2×10^{-2} mole/liter of $\underline{a}$ is allowed to equilibrate at 60°. What is the equilibrium concentration of $\underline{b}$ in moles per liter?

(Hint: Let the amount of $\underline{b}$ formed be equal to $\underline{x}$.)

A-32 At equilibrium

$$[\underline{b}] = \underline{x}$$

$$[\underline{a}] = [\underline{a}^\circ - \underline{x}]$$

where $\underline{a}^\circ$ = initial concentration of $\underline{a}$ (1.2×10^{-2} mole/liter).

$$K_{eq} = \frac{[\underline{b}]}{[\underline{a}]} = \frac{\underline{x}}{[\underline{a}^\circ - \underline{x}]} = 1.0 \times 10^{-4}$$

$$\frac{\underline{x}}{1.2 \times 10^{-2} - \underline{x}} = 1.0 \times 10^{-4}$$

$$\underline{x} = 1.2 \times 10^{-6} - 1.0 \times 10^{-4}(\underline{x})$$

$$(1 + 1.0 \times 10^{-4})\underline{x} = 1.2 \times 10^{-6}$$

$\underline{x} = 1.2 \times 10^{-6}$ M (two significant figures)

$$[\underline{b}] = \underline{x} = 1.2 \times 10^{-6}\ M$$

Q-33 The equilibrium constant for the reaction

$$\underline{e} + \underline{b} \rightleftarrows \underline{c} + \underline{d}$$

is 3.8×10^{-2} at 25°. When a solution 1.2×10^{-4} molar in $\underline{e}$ and 1.2×10^{-4} molar in $\underline{b}$ is allowed to equilibrate at 25°C, what is the equilibrium concentration of $\underline{c}$ and $\underline{d}$?

(Hint. Equations of the form

$$K = \frac{\underline{x}^2}{(1 - \underline{x})^2}$$

are more easily solved by taking square roots of both sides of the equation than by use of the quadratic equation.)

A-33 Let $\underline{x}$ = concentration of $\underline{c}$ at equilibrium Since one mole of $\underline{d}$ is formed for every mole of $\underline{c}$ produced, the concentration of $\underline{d}$ at equilibrium must also equal $\underline{x}$ For every mole of $\underline{e}$ which reacts, one mole of $\underline{b}$ must also react so that at equilibrium

$$[\underline{e}] = [\underline{e}^\circ - \underline{x}]$$

$$[\underline{b}] = [\underline{b}^\circ - \underline{x}]$$

$$[\underline{c}] = \underline{x} = [\underline{d}]$$

$$K_{eq} = \frac{[\underline{c}][\underline{d}]}{[\underline{e}][\underline{b}]} = 3\ 8 \times 10^{-2}$$

$$\frac{[\underline{c}][\underline{d}]}{[\underline{e}][\underline{b}]} = \frac{(\underline{x})(\underline{x})}{(1\ 2 \times 10^{-4} - \underline{x})(1\ 2 \times 10^{-4} - \underline{x})} = 3\ 8 \times 10^{-2}$$

Taking the square root of both sides

$$\frac{\underline{x}}{(1\ 2 \times 10^{-4} - \underline{x})} = \sqrt{3\ 8 \times 10^{-2}} = 0\ 19$$

$$1\ 2\underline{x} = 2\ 3 \times 10^{-5}$$

$$\underline{x} = [\underline{c}] = [\underline{d}] = 1\ 9 \times 10^{-5}\,M$$

Q-34 For the reaction

$$\underline{d} \rightleftharpoons \underline{e} + \underline{f}$$

the equilibrium constant is $5\ 0 \times 10^{-5}$ mole/liter at 25° A solution which is $1\ 0 \times 10^{-4}$ molar in $\underline{d}$ is allowed to equilibrate at 25° What would the equilibrium concentration of $\underline{f}$ be?

(Hint For $a\underline{x}^2 + b\underline{x} + c = 0$

$$\underline{x} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\ )$$

A-34 Let $\underline{x}$ = concentration of $\underline{f}$ at equilibrium Since one mole of $\underline{f}$ is produced for every mole of $\underline{e}$, the equilibrium concentration of both $\underline{e}$ and $\underline{f}$ will be $\underline{x}$, and the equilibrium concentration of $\underline{d}$ will be $[\underline{d}^\circ - \underline{x}]$

$$K_{eq} = \frac{[\underline{e}][\underline{f}]}{[\underline{d}]} = \frac{(\underline{x})(\underline{x})}{[\underline{d}^\circ - \underline{x}]} = 5\ 0 \times 10^{-5}\ \text{mole}/\ell$$

$$\underline{x}^2 + 5\ 0 \times 10^{-5}\underline{x} - 5\ 0 \times 10^{-9} = 0$$

Using the quadratic equation,

$$\underline{x} = \frac{-5\ 0 \times 10^{-5} \pm \sqrt{25 \times 10^{-10} - (4)(-5\ 0 \times 10^{-9})}}{2}$$

$$\underline{x} = [\underline{e}] = [\underline{f}] = 5\ 0 \times 10^{-5}\,M$$

Q-35 For the reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

the equilibrium constant is 46 at 490°C. If one mole of H_2 and I_2 were introduced into a liter vessel and equilibrated at 490°C, what would be the concentration of HI at equilibrium?

(Hint: If $\underline{x}$ is the amount of H_2 that reacts, what will [HI] be?)

A-35 If $\underline{x}$ = amount of H_2 that reacts, then at equilibrium

$$[H_2] = 1 - \underline{x}$$
$$[I_2] = 1 - \underline{x}$$
$$[HI] = 2\underline{x}$$
$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2\underline{x})^2}{(1-x)(1-x)}$$

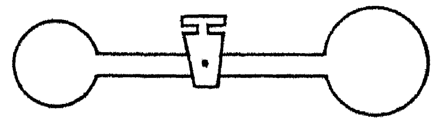
Taking the square root of both sides

$$\frac{2\underline{x}}{1-\underline{x}} = \sqrt{46} = 6\ 8$$
$$2\underline{x} = 6\ 8 - 6.8\underline{x}$$
$$9\underline{x} = 6\ 8$$
$$\underline{x} = 0\ 8\,M$$
$$[HI] = 2\,M$$
$$[H_2] = [I_2] = 0.2\,M$$

Q-36 A certain compound is prepared by allowing the following reaction to come to equilibrium

$$A_2 + B_2 \rightleftharpoons 2AB$$

All reactants and products are in the gas phase at 100° and at that temperature the equilibrium constant is 50 If a one liter vessel containing one mole of A_2 is connected to a 2 liter vessel containing 2 moles of B_2, and the gases are allowed to mix at 100°C, how many moles of AB will be produced?



(Hint Determine all concentrations in moles per liter.)

A-36 In this problem, the reaction vessel is 3 liters and contains initially 1 mole of $A_2(A_2^o)$ and 2 moles of $B_2(B_2^o)$

Therefore,

$$[A_2^o] = 1/3\,M$$
$$[B_2^o] = 2/3\,M$$

Let $\underline{x}$ = $[A_2]$ which reacts
= $[B_2]$ which reacts

Then

$2\underline{x}$ = [AB] produced by the reaction

$$K_{eq} = \frac{[AB]^2}{[A_2][B_2]} = \frac{(2\underline{x})^2}{(1/3-\underline{x})(2/3-\underline{x})} = 50$$
$$4\underline{x}^2 = 50(0.2 - \underline{x} + \underline{x}^2)$$
$$46\underline{x}^2 = 50\underline{x} + 10 = 0$$
$$\underline{x} = \frac{50 \pm \sqrt{25 \times 10^2 - (4)(46)(10)}}{2(46)} = 0.8 \text{ or } 0.3 \text{ (one significant figure)}$$

If $\underline{x}$ were 0.8 M, $[A_2]$ would be

0.3 - 0.8 = -0.5 mole/ℓ,
obviously a nonsensical answer.

Therefore,

$$\underline{x} = 0.3\,M$$
$$[AB] = 2\underline{x} = 0.6\,M$$

Because the volume of the vessel is 3 liters the total amount of AB produced must be 3(0.6) or 2 moles.

R **If the equilibrium constant is known for a reaction, it is possible to calculate the quantities of reactants and products present at equilibrium.**

PART II: Application of Equilibrium Theory

S-1 The theories developed in Part I will now be applied to solution equilibria

A list of strong and weak acids is given below Strong acids dissociate completely (or very nearly so) in aqueous solution while weak acids only partially dissociate The dissociation reaction for an acid, HA, is

$$HA \rightleftharpoons H^+ + A^-$$

strong acid	K_{eq}-mole/ℓ	weak acid	K_{eq}-mole/ℓ
hydrochloric acid (HCl)	greater than 1	acetic acid (CH_3COOH)	$1\ 9 \times 10^{-5}$
sulfuric acid (H_2SO_4)	greater than 1	benzoic acid (C_6H_5COOH)	$6\ 6 \times 10^{-5}$
hydroiodic acid (HI)	greater than 1	hydrocyanic acid (HCN)	$4\ 0 \times 10^{-10}$
perchloric acid ($HClO_4$)	greater than 1	hydrofluoric acid (HF)	$6\ 9 \times 10^{-4}$

Q-1 Hydrogen chloride is a strong acid which dissociates nearly completely in water according to the equation

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

What would be the value of the equilibrium constant?

(Hint What is the equilibrium concentration of HCl?)

A-1 The equilibrium expression for the reaction would be

$$K_{eq} = \frac{[H^+][Cl^-]}{[HCl]}$$

Because nearly all the HCl dissociates, [HCl] at equilibrium approaches zero and K_{eq} approaches infinity

Q-2 Strong acids (such as HCl) dissociate nearly completely in aqueous solution and the equilibrium constant is very large Weak acids only partially dissociate in water Which acid, hydrogen fluoride (HF) or hydrogen cyanide (HCN) is the weaker acid? Explain in terms of the equilibrium expression.

$$HF \rightleftharpoons H^+ + F^-$$

$$HCN \rightleftharpoons H^+ + CN^-$$

A-2 The weaker acid is HCN.

$$K_{HCN} = \frac{[H^+][CN^-]}{[HCN]} = 4\ 0 \times 10^{-10}\ \text{mole/ℓ}$$

$$K_{HF} = \frac{[H^+][F^-]}{[HF]} = 6\ 9 \times 10^{-4}\ \text{mole/ℓ}$$

The equilibrium constants indicate that the ratio of $[H^+][CN^-]$ to [HCN] is very much smaller than the ratio of $[H^+][F^-]$ to [HF]

Q-3 A weak acid, HA, dissociates according to the equation

$$HA \rightleftharpoons H^+ + A^-$$

A solution with the initial concentration of HA = 0 1 mole/liter was found to be 1% dissociated. What is the equilibrium constant?

(Hint· Find the equilibrium concentrations of reactants and products.) .

A-3 The acid is 1% dissociated Concentration of HA which dissociates

$= [HA] (0\ 01)$

$= [0\ 1] (0.01) = 0\ 001$ mole/ℓ

Therefore,

$[H^+] = 0\ 001\ M$

$[A^-] = 0\ 001\ M$

$[HA] = (0\ 1 - 0\ 001)\ M$

$$K_{eq} = \frac{[H^+][A^-]}{[HA]} = \frac{(0\ 001)(0\ 001)}{(0\ 1 - 0\ 001)} = 1 \times 10^{-5} \text{ mole/ℓ}$$

A-4 Acetic acid (abbreviated as HAc) dissociates according to the equation

$$HAc \rightleftharpoons H^+ + Ac^-$$

The dissociation (equilibrium) constant for the acid is $1\ 90 \times 10^{-5}$ mole/ℓ . In a solution of HAc, the equilibrium concentration of H^+ was found to be 4.5×10^{-5} mole/liter What is the concentration of undissociated acetic acid, i. e , HAc?

A-4 At equilibrium

$[H^+] = 4.5 \times 10^{-5}\ M$

Since an Ac^- ion is produced for every H^+ ion,

$[Ac^-] = 4.5 \times 10^{-5}\ M$

$$K_{eq} = \frac{[H^+][Ac^-]}{[HAc]} = \frac{(4.5 \times 10^{-5})^2}{[HAc]} = 1.9 \times 10^{-5} \text{ mole/ℓ}$$

$$[HAc] = \frac{(4.5 \times 10^{-5})^2}{1.9 \times 10^{-5}} = 1\ 1 \times 10^{-4}\ M$$

[redacted]

S-2 In solving equilibrium problems, it is sometimes possible to make approximations which simplify the mathematics but do not affect the numerical answer. For example, a 0 10 mole sample of a weak acid (HA) ($K_{HA} = 1.0 \times 10^{-7}$), is dissolved in enough water to make a liter of solution and dissociates according to the equation

$$HA \rightleftharpoons H^+ + A^-$$

To find $[H^+]$, let $\underline{x}$ equal the amount of H formed, then

$[H^+] = \underline{x}$

$[A^-] = \underline{x}$

$[HA] = 0.10 - \underline{x}$

and

$$K_{HA} = \frac{[H^+][A^-]}{[HA]} = \frac{(\underline{x})(\underline{x})}{(0.10 - \underline{x})}$$

The exact method of solution requires the use of the quadratic equation. The approximate method of solution avoids the use of the quadratic equation and employs the following reasoning. HA will dissociate very little (K is very small). Therefore, $\underline{x}$ will be very small compared to the amount of HA present. Approximate $0.10 - \underline{x}$ as 0.10.

$$1.0 \times 10^{-7} = \frac{\underline{x}^2}{0.10} \qquad \underline{x} = 1.0 \times 10^{-4}\,M$$

Therefore, the approximation made, $0.10 - \underline{x} = 0.10$ was valid

Using the quadratic yields the same answer i.e.,

$$1.0 \times 10^{-7} = \frac{\underline{x}^2}{(0.10 - \underline{x})}$$

$$\underline{x}^2 + 1.0 \times 10^{-7}\underline{x} - 1.0 \times 10^{-8} = 0$$

$$\underline{x} = \frac{-1.0 \times 10^{-7} \pm \sqrt{(1.0 \times 10^{-7})^2 - (4)(1)(-1.0 \times 10^{-8})}}{2}$$

because 1.0×10^{-14} is much smaller than 4.0×10^{-8}, the value of the square root is 2.0×10^{-4}

$$\underline{x} = \frac{-1.0 \times 10^{-7} \pm 2.0 \times 10^{-4}}{2}$$

$\underline{x} = 1.0 \times 10^{-4}$ (two significant figures)

Q-5 A weak acid dissociates according to the following equation

$$HA \rightleftharpoons H^+ + A^-$$

If the equilibrium constant is 2.0×10^{-5} mole/ℓ, what is $[H^+]$ in a solution prepared by diluting 0.10 mole of HA to 1.0 liter with water?

A-5 The initial concentration of HA(HA°) is 0.10 mole/liter. Let $\underline{x}$ = the amount of HA that dissociates. Then,

$$[H^+] = \underline{x}$$

$$[A^-] = \underline{x}$$

$$[HA] = [HA^\circ - \underline{x}]$$

$$K_{eq} = \frac{[H^+][A^-]}{[HA]} = \frac{(\underline{x})(\underline{x})}{[HA^\circ - \underline{x}]} = 2.0 \times 10^{-5}\ \text{mole/ℓ}$$

$$\frac{\underline{x}^2}{0.10 - \underline{x}} = 2.0 \times 10^{-5}$$

The concentration of HA° is known to only two significant figures. Because K_{eq} is 2.0×10^{-5}, only a small amount of HA dissociates. Assume that $\underline{x} \lll 0.10$ ($\underline{x}$ is much smaller than 0.10) and test to see if the approximation is valid. Making the approximation,

$$\frac{\underline{x}^2}{0.10} = 2.0 \times 10^{-5}$$

$$\underline{x}^2 = 2.0 \times 10^{-6}$$

$$\underline{x} = [H^+] = 1.4 \times 10^{-3}\,M$$

Now subtract 1.4×10^{-3} from 0.10 (which would have been done if the approximation had not been made) and round off to two significant figure. The value is still 0.10, this indicates that the original approximation was valid and saved the trouble of solving a quadratic equation.

Q-6 Consider the weak acid of the preceding question. A solution was made up by diluting 0.0010 mole of HA to one liter. If the $[H^+]$ was to be determined, could the same approximation be made in calculating the answer as in the previous case? Why?

A-6 Write the equilibrium expression

$$\frac{\underline{x}^2}{0.0010 - \underline{x}} = 2.0 \times 10^{-5}$$

By assuming that $\underline{x} <<< 0\ 0010$, the value found for $\underline{x}$ is $1\ 4 \times 10^{-4}$ Now subtracting 1.4×10^{-4} from 0 0010 yields 0 0009. In this case, it would be much better not to make the approximation as this would change the answer somewhat

Q-7 Consider the weak acid HAc which dissociates according to the equation

$$HAc \rightleftharpoons H^+ + A^-$$

The equilibrium constant for this reaction is $1\ 9 \times 10^{-5}$ mole/ℓ What will the $[H^+]$ be in a solution prepared by diluting 0 100 mole HAc to one liter with water? (Let $\underline{x}$ = mole/liter of HAc which dissociate The HAc dissolves completely)

A-7

$$K_{eq} = \frac{[H^+][Ac^-]}{[HAc]} = \frac{(\underline{x})(\underline{x})}{0\ 100 - \underline{x}} = 1\ 9 \times 10^{-5} \text{ mole/ℓ}$$

assuming $\underline{x} <<< 0\ 100$,

$$\underline{x}^2 = 1.9 \times 10^{-6}$$

and $\underline{x} = 1\ 4 \times 10^{-3}\,M = [H^+] = [Ac^-]$

Q-8 What is the $[H^+]$ in a solution prepared by adding 0.1 mole HCN to a liter of H_2O? (The HCN dissolves completely)

A-8 $HCN \rightleftharpoons H^+ + CN^-$

$$K_{HCN} = \frac{[H^+][CN^-]}{[HCN]} = 4\ 0 \times 10^{-10} \text{mole/ℓ}$$

Let $\underline{x} = [H^+] = [CN^-]$

Therefore,

$[HCN] = 0.1 - \underline{x}$

If $\underline{x} <<< 0\ 1$, then the equilibrium expression can be written

$$\frac{\underline{x}^2}{0.1} = 4.0 \times 10^{-10}$$

$\underline{x} = 6 \times 10^{-6}\,M = [H^+]$

Q-9 The equilibrium constants for HCN and HAc are $4\ 0 \times 10^{-10}$ and $1\ 9 \times 10^{-5}$ mole/ℓ, respectively. Which acid is stronger? What are the concentrations of H^+ ion in 0.1 molar solutions of these two acids? (See A-7 and A-8.)

A-9 Acetic acid is the stronger acid.

$[H^+]$ in 0 1 M HAc = 1×10^{-3} M

$[H^+]$ in 0.1 M HCN = 6×10^{-6} M

Q-10 A solution is prepared by dissolving 1 0 mole of HF in a liter of water What is the H^+ ion concentration in this solution? ($K_{HF} = 6.9 \times 10^{-4}$ mole/ℓ.)

A-10

$$K_{HF} = \frac{[H^+][F^-]}{[HF]} = 6\ 9 \times 10^{-4} \text{ mole/ℓ}$$

Let $\underline{x} = [H^+] = [F^-]$

Then,

$$[HF] = 1.0 - \underline{x}$$

If $\underline{x} <<< 1\ 0$

$$[HF] = 1.0\,M$$

Then,

$$\frac{\underline{x}^2}{1.0} = 6.9 \times 10^{-4}$$

$$\underline{x} = 2.6 \times 10^{-2}\,M = [H^+]$$

To check the approximation, note that $1.0 - 0.026 = 1.0$

R **When <u>subtracting</u> or <u>adding</u> a relatively small number from a large number, the sum or difference can be approximated by neglecting the smaller number. Such approximations should be used only if the numerical answer of the problem is unaffected by the approximation.**

S-3 The ionization of diprotic acids, such as H_2S and H_2CO_3, involves two ionization steps

$$H_2S \rightleftarrows H^+ + HS^- \qquad K_1 = 1.0 \times 10^{-7} \text{ mole}/\ell$$

$$HS^- \rightleftarrows H^+ + S^{-2} \qquad K_2 = 1.3 \times 10^{-13} \text{ mole}/\ell$$

For most diprotic acids, the second ionization constant (K_2) is <u>smaller</u> by approximately five powers of ten (10^5)

Q-11 A solution is 0.100 M in H_2S. Which ion, HS^- or S^{-2}, will be present in the larger concentration? How do you know?

A-11 HS^- will be present in the larger concentration. The dissociation constant for HS^-(K_2) is very small indicating that very little of the HS^- which formed will dissociate

Q-12 A 0.100 M solution of H_2S is acidic. What has been the main source of the excess protons, the dissociation of H_2S or the dissociation of HS^-? How do you know?

A-12 The dissociation of H_2S. K_1 is much larger than K_2, therefore, very few protons are formed by the dissociation of HS^- as compared to the number formed in the dissociation of H_2S

Q-13 In a 0.100 M solution of H_2S will $[H^+]$ be approximately equal to $[HS^-]$ or twice $[S^{-2}]$? How do you know?

A-13 $[H^+]$ is approximately equal to $[HS^-]$. Very little HS^- dissociates so very little H^+ is formed in the second ionization step

Q-14 What is the approximate value of $[H^+]$ and $[HS^-]$ in a 0.100 M solution of H_2S? (Hint: Let $\underline{x}$ = $[H^+]$ at equilibrium.)

A-14 $K_1 = \dfrac{[H^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7}$ mole/ℓ

At equilibrium

$\underline{x} = [H^+] = [HS^-]$ approximately

$[H_2S] = 0.100 - \underline{x}$

If $\underline{x} \lll 0.100$, then

$\dfrac{x^2}{(0.100)} = 1.0 \times 10^{-7}$

$\underline{x} = 1.0 \times 10^{-4}\,M = [H^+] = [HS^-]$

Q-15 If a 0.100 M H_2S solution is 1.0×10^{-4} M in H^+ and HS^-, what is the concentration of S^{-2} in mole/liter?

$K_2 = \dfrac{[H^+][S^{-2}]}{[HS^-]} = 1.3 \times 10^{-13}$ mole/ℓ

A-15 $K_2 = \dfrac{[H^+][S^{-2}]}{[HS^-]} = 1.3 \times 10^{-13}$ mole/ℓ

$[H^+] = [HS^-]$ approximately,

Therefore,

$K_2 = [S^{-2}] = 1.3 \times 10^{-13}$ mole/ℓ

Q-16 If $[H^+]$ and $[HS^-]$ were 1.0×10^{-4} M before dissociation of HS^- occurred and the true value of $[S^{-2}]$ is 1.3×10^{-13} M, what would the true value of $[H^+]$ and $[HS^-]$ be?

A-16 $[H^+] = 1.0 \times 10^{-4}\,M + 1.3 \times 10^{-13}\,M$

$[HS^-] = 1.0 \times 10^{-4}\,M - 1.3 \times 10^{-13}\,M$

Q-17 An H_2S solution was found to be $1.0 \times 10^{-3}\,M$ in H_2S. What is $[HS^-]$ and $[S^{-2}]$ in the solution?

A-17 $$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7}\ \text{mole}/\ell$$

Let $\underline{x} = [HS^-]$

$[H^+] = [HS^-]$ approximately and

$\underline{x} <<< [H_2S]$

$$\frac{x^2}{1.0 \times 10^{-3}} = 1.0 \times 10^{-7}$$

$\underline{x} = 1.0 \times 10^{-5}\,M = [HS^-]$

$$K_2 = \frac{[H^+][S^{-2}]}{[HS^-]} = 1.3 \times 10^{-13}\ \text{mole}/\ell$$

if $[H^+] = [HS^-]$

Then,

$[S^{-2}] = 1.3 \times 10^{-13}\,M$

Note that $[S^{-2}]$ changes very little as $[H_2S]$ changes

Q-18 The first ionization constant for carbonic acid is 4.2×10^{-7} mole/ℓ

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

What will the approximate ionization constant of HCO_3^- be?

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}.$$

A-18 Approximately 4×10^{-12}

K_2 is actually 4.8×10^{-11}.

Q-19 A solution is saturated with carbonic acid ($[H_2CO_3] = 0.034\,M$). Will $[HCO_3^-]$ be larger, equal to or less than $[CO_3^{-2}]$ in the solution? How do you know?

$K_1 = 4.2 \times 10^{-7}$ mole/ℓ

$K_2 = 4.8 \times 10^{-11}$ mole/ℓ

A-19 $[HCO_3^-] >>> [CO_3^{-2}]$

K_2 is very small, so very little HCO_3^- dissociates.

Q-20 What will be the approximate concentration of H^+ and HCO_3^- in a saturated (0.034 M) solution of H_2CO_3?

A-20 $$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.2 \times 10^{-7}\ \text{mole}/\ell$$

Let $\underline{x} = [H^+]$ at equilibrium

Approximately, $[H^+] = [HCO_3^-] = \underline{x}$

$\underline{x} <<< [H_2CO_3]$

$$\frac{x^2}{0.034} = 4.2 \times 10^{-7}$$

$\underline{x}^2 = 1.4 \times 10^{-8}$

$\underline{x} = 1.2 \times 10^{-4}\,M = [H^+] = [HCO_3^-]$

Q-21 What is the approximate concentration of CO_3^{-2} in a saturated H_2CO_3 solution?

A-21 In a saturated H_2CO_3 solution

$$[H^+] = [HCO_3^-] \text{ (approximately)}$$

$$K_2 = \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]} = 4.8 \times 10^{-11} \text{ mole}/\ell$$

$$[CO_3^{-2}] = 4.8 \times 10^{-11} \text{ M}$$

R For diprotic acids such as H_2S and H_2CO_3, the first ionization constant is larger (by about 10^5) than the second ionization constant. Therefore, [anion from first ionization] >>> [anion from second ionization]. For example, $[HS^-] >>>> [S^{-2}]$.

S-4 In a homogeneous reaction, all components are in a single phase That is, all reactants and products are in solution, or all are in the gaseous state Reactions in which all of the components are not in a single phase are called heterogeneous reactions For example, in a saturated silver chloride solution containing some solid AgCl, the equilibrium is

$$AgCl_{(s)} \rightleftarrows Ag^+_{(\text{in solution})} + Cl^-_{(\text{in solution})}$$

For this reaction the equilibrium expression is

$$K_{eq} = \frac{[Ag^+][Cl^-]}{[AgCl_{(s)}]}$$

Unlike the homogeneous equilibrium, addition of more solid AgCl will not cause any change in concentration of silver ions in solution The term $[AgCl_S]$ is a constant because the concentration of any compound in the solid state is independent of the amount of solid present The concentration of a solid is found by dividing density by the molecular weight.

$$\text{concentration in solid} = \frac{\text{density}}{\text{molecular weight}} = \frac{(\text{gm/cc})}{(\text{gm/mole})} = \frac{\text{mole}}{\text{cc}}$$

Because both the density and the molecular weight of a solid are constants, the concentration must be a constant Because $[AgCl_S]$ is a constant, a new equilibrium expression can be written

$$[AgCl]K_{eq} = [Ag^+][Cl^-] = K_{sp}$$

K_{sp} is called the solubility product constant

Q-22 The solubility of AgCl in water at 10°C is 6.2×10^{-6} mole/liter. What is the value of K_{sp} for AgCl?

(Hint: $[Ag^+]$ is 6.2×10^{-6} M)

A-22 $AgCl \rightleftarrows Ag^+ + Cl^-$

For every mole of AgCl which dissolves, a mole of Ag^+ ions and Cl^- ions forms. Therefore, in a saturated solution of AgCl, $[Ag^+] = 6.2 \times 10^{-6}M = [Cl^-]$

$$K_{sp} = [Ag^+][Cl^-]$$
$$= (6.2 \times 10^{-6})^2 = 3.8 \times 10^{-11} \text{mole}^2/\ell^2$$

Q-23 The solubility of NaCl in water at 10°C is 6.1 mole/liter. What is the value of K_{sp} for NaCl?

A-23 In a saturated solution of NaCl,

$$[Na^+] = [Cl^-] = 6.1 \text{ M}$$

$$K_{sp} = [Na^+][Cl^-]$$
$$= (6.1)^2 = 37 \text{ mole}^2/\ell^2$$

Q-24 The terms soluble and insoluble are often used in describing the solubility characteristics of salts. In terms of K_{sp}, what is implied by the words soluble and insoluble? How would NaCl and AgCl be classified?

A-24 A soluble salt is one which has a large K_{sp} value (approximately 1 or greater) while an insoluble salt has a very small value for K_{sp}

The K_{sp} for AgCl is very small (3.8×10^{-11} mole$^2/\ell^2$) while the K_{sp} for NaCl is comparatively large (37 mole$^2/\ell^2$) AgCl is considered an insoluble salt while NaCl is considered a soluble salt

Q-25 The K_{sp} for the salt CuCl is

$$3.2 \times 10^{-7} \text{ mole}^2/\ell^2$$

What is the concentration of Cu^+ ions in a saturated solution of CuCl?

(Hint Let $\underline{x} = [Cu^+]$)

A-25 $CuCl \rightleftharpoons Cu^+ + Cl^-$

$K_{sp(CuCl)} = [Cu^+][Cl^-]$

In a saturated solution

$[Cu^+] = [Cl^-]$

Let $\underline{x} = [Cu^+]$

$\underline{x}^2 = 3.2 \times 10^{-7}$

$\underline{x} = 5.7 \times 10^{-4} M = [Cu^+]$

Q-26 A saturated solution of cupric carbonate ($CuCO_3$) is prepared

$$K_{sp} = 2.5 \times 10^{-10} \text{ mole}^2/\ell^2$$

What is $[Cu^{+2}]$ in this solution?

A-26 $CuCO_3 \rightleftharpoons Cu^{+2} + CO_3^{-2}$

$K_{sp} = [Cu^{+2}][CO_3^{-2}] = 2.5 \times 10^{-10}$ mole$^2/\ell^2$

Let $x = [Cu^{+2}] = [CO_3^{-2}]$

$\underline{x}^2 = 2.5 \times 10^{-10}$

$\underline{x} = 1.6 \times 10^{-5} M$

Q-27 The K_{sp} of barium oxalate (BaC_2O_4) is 1.5×10^{-8} mole$^2/\ell^2$. The equilibrium involved is

$$BaC_2O_4 \rightleftharpoons Ba^{+2} + C_2O_4^{-2}$$

If a solution is saturated with barium oxalate, what is the oxalate concentration in mole/liter?

A-27 $K_{sp} = [Ba^{+2}][C_2O_4^{-2}]$

Let $\underline{x}$ = concentration of Ba^{+2} in mole/liter. Then,

$[Ba^{+2}] = \underline{x}$

$[C_2O_4^{-2}] = \underline{x}$

$K_{sp} = \underline{x}^2 = 1.5 \times 10^{-8}$ mole$^2/\ell^2$

$\underline{x} = 1.2 \times 10^{-4} M = [C_2O_4^{-2}]$

Q-28 The solubility of strontium fluoride (SrF_2) in water at 25° is 5.82×10^{-4} mole/liter. What is K_{sp} for SrF_2?

A-28 $SrF_2 \rightleftharpoons Sr^{+2} + 2F^-$

If 5.82×10^{-4} mole of SrF_2 dissolve in 1 liter of H_2O, then

$[Sr^{+2}] = 5.82 \times 10^{-4} M$.

Since two F^- form for every Sr^{+2}

$[F^-] = 2(5.82 \times 10^{-4})M = 11.6 \times 10^{-4} M$

$K_{sp} = [Sr^{+2}][F^-]^2$

$= (5.82 \times 10^{-4})(11.6 \times 10^{-4})^2$

$= 7.83 \times 10^{-10}$ mole$^3/\ell^3$

Q-29 The solubility product of manganic oxalate, $Mn_2(C_2O_4)_3$, is 7×10^{-20} mole$^5/\ell^5$. Write the solubility product expression.

$Mn_2(C_2O_4)_3 \rightleftharpoons 2Mn^{+3} + 3C_2O_4^{-2}$

A-29 $K_{sp} = [Mn^{+3}]^2[C_2O_4^{-2}]^3 = 7 \times 10^{-20}\ mole^5/\ell^5$

Q-30 How many moles of manganic hydroxide, $Mn(OH)_3$ would dissolve in 1 liter of water?

K_{sp} for $Mn(OH)_3$ = 1 0 x $10^{-36}\ mole^4/\ell^4$

$$Mn(OH)_3 \rightarrow Mn^{+3} + 3OH^-$$

(Hint. Write out the reaction and the solubility product expression. Let $\underline{x}$ = moles of $Mn(OH)_3$ which dissolve)

A-30 $Mn(OH)_3 \rightleftharpoons Mn^{+3} + 3OH^-$

$K_{sp} = [Mn^{+3}]\,[OH^-]^3$

If $\underline{x}$ = moles of $Mn(OH)_3$ which dissolve

$\underline{x} = [Mn^{+3}]$ and $3x = [OH^-]$

$K_{sp} = (\underline{x})(3\underline{x})^3 = 27x^4 = 1 \times 10^{-36}\ mole^4/\ell^4$

$\underline{x} = \sqrt[4]{1/27} \times \sqrt[4]{10^{-36}}$

$= 4\ 4 \times 10^{-10}\,M$

Q-31 Magnesium hydroxide has a K_{sp} of $8\ 9 \times 10^{-12}\ mole^3/\ell^3$

What is the pH of a saturated solution of $Mg(OH)_2$ at 25° The equilibrium is

$$Mg(OH)_2 \rightleftharpoons 2OH^- + Mg^{+2}$$

Assume an activity coefficient of one

[Hint pH = - log (activity coefficient x $[H^+]$)

pH + pOH = 14 00 at 25°]

A-31 $K_{sp} = [Mg^{+2}]\,[OH^-]^2$

If $\underline{x} = [Mg^{+2}]$, then $[OH^-] = 2\underline{x}$

$(\underline{x})(2\underline{x})^2 = 8.9 \times 10^{-12}\ mole^3/\ell^3$

$\underline{x} = 1\ 3 \times 10^{-4}\,M$

$[OH^-] = 2.6 \times 10^{-4}\,M$

pOH = 3 59

pH = 14 00 - 3 59 = 10.41

R For a salt M_mX_n, dissolved in water, $K_{sp} = [M]^m[X]^n$.

S-5 When a common species is added to a reaction in equilibrium, a change in the equilibrium concentrations occurs Le Chatelier's rule predicts qualitatively the direction in which the equilibrium will shift The equilibrium expression allows the quantitative description of the change in equilibrium position.

Q-32 The concentration of Ac^- ion present in a 0 100 molar solution of acetic acid was found to be 1.36×10^{-3} mole/liter.

$$HAc \rightleftharpoons H^+ + Ac^-$$

If 0.0100 mole of HCl is added to one liter of a 0.100 molar acetic acid solution, would the $[Ac^-]$ be expected to be greater than or less than 1.36×10^{-3} M? Why?

A-32 Less than. Le Chatelier's rule would predict that the reaction would shift to the left because increasing the H^+ ion concentration places a stress on the system.

Q-33 **For the solution described in the previous question, if $\underline{x}$ is equal to the amount of HAc that dissociates, what will be the values for $[Ac^-]$, $[H^+]$, and $[HAc]$ at equilibrium in terms of $\underline{x}$?**

(Hint: HCl is completely dissociated.)

A-33 $[Ac^-] = \underline{x}$

$[HAc] = 0\ 100 - \underline{x}$

$[H^+] = 0.0100$ (from the HCl) + $\underline{x}$ (from the HAc which dissociated)

Q-34 Using the values determined for the previous question, calculate $[Ac^-]$ for the solution described

$$K_{eq} = 1.9 \times 10^{-5}\ \text{mole}/\ell$$

(Hint Can any approximations be made?)

A-34 $$K_{eq} = \frac{[H^+][Ac^-]}{[HAc]} = \frac{(0.0100 + \underline{x})(\underline{x})}{(0\ 100 - x)}$$

The approximations made are

$\underline{x} <<< 0.100$, $\underline{x} << 0.0100$

$\underline{x} = [Ac^-] = 1.9 \times 10^{-4}\ M$

Note that $[Ac^-]$ was predicted from Le Chatelier's rule to be less than $1\ 36 \times 10^{-3}\ M$

Q-35 A solution is prepared by diluting 0 30 mole of HAc and 0 15 mole of HCl to one liter. Express the values for $[Ac^-]$, $[HAc]$ and $[H^+]$ at equilibrium in terms of $\underline{x}$, the amount of HAc which dissociates

A-35 Letting $\underline{x}$ equal the amount of HAc that dissociates, the values are

$[Ac^-] = \underline{x}$

$[HAc] = 0\ 30 - \underline{x}$

$[H^+] = 0\ 15 + \underline{x}$

Q-36 For the aqueous solution described in the previous question, calculate the values for $[Ac^-]$, $[HAc]$ and $[H^+]$.

$$K_{HAc} = 1.9 \times 10^{-5}\ \text{mole}/\ell$$

A-36 At equilibrium

$[Ac^-] = \underline{x}$

$[HAc] = 0.30 - \underline{x}$

$[H^+] = 0\ 15 + \underline{x}$

Approximating that $\underline{x} << 0\ 30$ and 0.15

$$K_{eq} = \frac{(0.15)(\underline{x})}{(0.30)} = 1.9 \times 10^{-5}\ \text{mole}/\ell$$

$[Ac^-] = \underline{x} = 3\ 8 \times 10^{-5}\ M$

$[HAc] = 0.30 - \underline{x} = 0.30\ M$

$[H^+] = 0.15 + \underline{x} = 0.15\ M$

Q-37 In a 0.100 M solution of H_2S, $[HS^-]$ and $[H^+]$ are

1.0×10^{-4} mole/liter.

If such a solution is made 0.10 M in H^+ ion (by the addition of HCl), how will $[HS^-]$ change?

$$K_{1(H_2S)} = 1.0 \times 10^{-7}\ \text{mole}/\ell.$$

A-37 $H_2S \rightleftharpoons H^+ + HS^-$

Addition of H^+ will shift the reaction to the left. Let $\underline{x} = [HS^-]$.

At equilibrium,

$[H_2S] = 0.100\ M - \underline{x}$

$[HS^-] = \underline{x}$

$[H^+] = 0.100\ M + \underline{x}$

Assume $\underline{x} <<< 0.100$

$$\frac{[H^+][HS^-]}{[H_2S]} = \frac{(0.100)(\underline{x})}{(0.100)} = 1.0 \times 10^{-7}\ \text{mole}/\ell$$

$\underline{x} = 1.0 \times 10^{-7} = [HS^-]_{final}$

Q-38 A 0 100 M H_2S solution containing 0.100 mole H^+ ion has a HS^- ion concentration of 1.0×10^{-7} M.

What is $[S^{-2}]$ in this solution?

$$K_{2(H_2S)} = 1.3 \times 10^{-13}\ \text{mole}/\ell$$

A-38 $K_2 = \dfrac{[H^+][S^{-2}]}{[HS^-]} = 1.3 \times 10^{-13}$ mole/ℓ

At equilibrium

$[H^+] = 0.100\,M$

$[HS^-] = 1.0 \times 10^{-7}\,M$

$[S^{-2}] = \dfrac{(1.3 \times 10^{-13})(1.0 \times 10^{-7})}{(0.100)}$

$= 1.3 \times 10^{-19}\,M$

Q-39 Combine the two equilibrium expressions

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7}\ \text{mole}/\ell$$

$$K_2 = \frac{[H^+][S^{-2}]}{[HS^-]} = 1.3 \times 10^{-13}\ \text{mole}/\ell$$

into a single equation by eliminating the term, $[HS^-]$

(Hint: Solve for $[HS^-]$ in each equation.)

A-39 $[HS^-] = \dfrac{[H_2S]\,K_1}{[H^+]}$

$[HS^-] = \dfrac{[H^+][S^{-2}]}{K_2}$

Therefore,

$\dfrac{[H_2S]\,K_1}{[H^+]} = \dfrac{[H^+][S^{-2}]}{K_2}$

$K_1K_2 = \dfrac{[H^+]^2[S^{-2}]}{[H_2S]} = 1.3 \times 10^{-20}\ \text{mole}^2/\ell^2$

Q-40 Using the equation developed in A-39, determine $[S^{-2}]$ for the solution described in Q-38.

A-40 $K_1K_2 = \dfrac{[H^+]^2[S^{-2}]}{[H_2S]}$

$K_1K_2 = 1.3 \times 10^{-20}\ \text{mole}^2/\ell^2$

$[H^+] = 0.100\,M$

$[H_2S] = 0.100\,M$

Therefore,

$[S^{-2}] = \dfrac{(1.3 \times 10^{-20})(0.100)}{(0.100)^2}$

$[S^{-2}] = 1.3 \times 10^{-19}\,M$

Q-41 What will $[S^{-2}]$ be in a solution 0.100 M in H_2S and 0.0010 M in H^+ ion?

Use the combined equation developed in A-39.

A-41 At equilibrium

$[H^+] = 1.0 \times 10^{-3}\,M$

$[H_2S] = 0.100\,M$

$K_1K_2 = \dfrac{[H^+]^2[S^{-2}]}{[H_2S]}$

$\dfrac{(1.0 \times 10^{-6})[S^{-2}]}{0.100} = 1.3 \times 10^{-20}$

$[S^{-2}] = 1.3 \times 10^{-15}\,M$

Q-42 **A certain metal sulfide, MS, has a solubility product constant (K_{sp}) of 1.3×10^{-18} mole²/ℓ². What must $[S^{-2}]$ be in a 0.10 M solution of M^{+2} when MS just starts to precipitate?**

A-42 $K_{sp} = [M^{+2}][S^{-2}] = 1.3 \times 10^{-18}\ \text{mole}^2/\ell^2$

$(0.10)[S^{-2}] = 1.3 \times 10^{-18}$

$[S^{-2}] = 1.3 \times 10^{-17}\,M$

Q-43 **If a solution was made 0.10 M in M^{+2} and 0.10 M in H_2S, what must $[H^+]$ be in order to just start the precipitation of MS?**

(Hint: See A-42.)

A-43 When precipitation occurs

$$[S^{-2}] = 1\ 3 \times 10^{-17} M$$

$$[H_2S] = 0\ 10 M$$

$$K_1K_2 = \frac{[H^+]^2[S^{-2}]}{[H_2S]}$$

$$\frac{[H^+]^2(1\ 3 \times 10^{-17})}{0\ 10} = 1\ 3 \times 10^{-20} \text{mole}^2/\ell^2$$

$$[H^+]^2 = 1.0 \times 10^{-4} M^2$$

$$[H^+] = 1\ 0 \times 10^{-2} M$$

Q-44 In a solution 0 100 M in H_2S and H^+ ion, $[S^{-2}]$ is 1 3 x 10^{-19} M (see A-38) In a solution 0 100 M in H_2S and 0 0010 M in H^+ ion, $[S^{-2}]$ is 1.3 x 10^{-15} M (see A-41) Is this consistent with Le Chatelier's rule?

$$H_2S \rightleftharpoons 2H^+ + S^{-2}$$

A-44 Yes LeChatelier's rule predicts that decreasing $[H^+]$ would increase the amount of H_2S dissociated and the concentration of S^{-2}

Q-45 A solution is made by diluting 0.10 mole HAc and 0 10 mole of the salt NaAc (which completely dissociates into Na+ and Ac^-) to one liter. What will be the $[H^+]$ at equilibrium?

(Hint: What will $[Ac^-]$ be? Remember some Ac^- comes from the HAc but 0.10 mole comes from the NaAc)

$$K_{HAc} = 1.9 \times 10^{-5} \text{ mole}/\ell$$

A-45 Let $\underline{x}$ = the mole/liter of HAc which dissociates.

Then, at equilibrium

$$\underline{x} = [H^+]$$

$$[Ac^-] = \underline{x} + 0.10$$

That is, $[Ac^-]$ = $[Ac^-]$ from dissociation of HAc + $[Ac^-]$ from the NaAc added.

$$K_{eq} = \frac{[H^+][Ac^-]}{[HAc]} = 1.9 \times 10^{-5} \text{ mole}/\ell$$

$$= \frac{(\underline{x})(0.10 + \underline{x})}{0.10 - \underline{x}}$$

Making the assumption that $\underline{x} << 0.1$, the equation becomes

$$\frac{(\underline{x})(0.10)}{0.10} = 1.9 \times 10^{-5}$$

$$\underline{x} = 1.9 \times 10^{-5} M = [H^+]$$

Has the addition of NaAc to a 0.1 molar solution of HAc increased or decreased $[H^+]$? See A-7.

Q-46 In a 0.10 M HAc solution, the amount of HAc which dissociates is 1.36 x 10^{-3} mole/liter if no other reagents are added. If 0.10 mole of NaAc or 0 10 mole of HCl is added, the amount of HAc which dissociates is 1 9 x 10^{-5} mole/liter. Is this consistent with Le Chatelier's rule? Why?

A-46 Yes. The equilibrium involved is

$$HAc \rightleftharpoons H^+ + Ac^-$$

If H^+ (as HCl) or Ac^- (as NaAc) is added, the rate of the reverse reaction increases, causing more HAc to form. Thus, less HAc will be dissociated.

Q-47 If a solution is made up containing 0.100 mole/liter of HAc and 0.100 mole/liter of NaAc and then 0.001 mole of HCl is added, does the $[H^+]$ increase by 0.001 mole/liter? Why? (Give only a qualitative answer.)

A-47 No. If the equilibrium

$$Na^+ + Ac^- + HAc \rightleftarrows 2Ac^- + H^+ + Na^+$$

has been established and H^+ ions are added, the reaction will shift to the left and in doing so, H^+ will be consumed. Therefore, if 0.001 mole of HCl is added to the system, the concentration of H^+ will not increase by 0.001 mole/liter, but something less than this.

Q-48 A solution of a weak acid (such as HAc) and a salt of the acid (NaAc) is called a <u>buffer</u>. Such solutions tend to resist change in $[H^+]$. A buffer is made from HAc($K = 1.9 \times 10^{-5}$ mole/ℓ) and NaAc. What must the ratio, $[Ac^-]/[HAc]$, be in order that $[H^+]$ be equal to 4.0×10^{-5}M?

A-48 $$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]} = 1.9 \times 10^{-5} \text{ mole/ℓ}$$

If $[H^+]$ is to be 4.0×10^{-5}M, then

$$\frac{[Ac^-]}{[HAc]} = \frac{1.9 \times 10^{-5}}{4.0 \times 10^{-5}} = 0.48$$

Q-49 Oxalic acid (which will be written as HOx) is a weak acid which dissociates according to the equation

$$HOx \rightleftarrows H^+ + Ox^-$$

The K_{eq} is 3.8×10^{-2} mole/ℓ. What would be the $[H^+]$ of a buffer containing 0.100 mole of oxalic acid and 0.100 mole of sodium oxalate (NaOx) per liter of solution (NaOx completely dissociates)?

(Hint: Let $\underline{x}$ = mole/liter of oxalic acid which dissociates.)

A-49 $$K_{HOx} = \frac{[H^+][Ox^-]}{[HOx]} = \frac{(\underline{x})(0.100 + \underline{x})}{(0.100 - x)} = 3.8 \times 10^{-2} \text{ mole/ℓ}$$

In this case, K_{eq} is not very small, so the assumption $\underline{x} <<< 0.1$ should <u>not</u> be made.

$$3.8 \times 10^{-3} - 3.8 \times 10^{-2}\underline{x} = 0.100\underline{x} + \underline{x}^2$$

or $\underline{x}^2 + 0.138\underline{x} - 3.8 \times 10^{-3} = 0$

$$\underline{x} = \frac{-0.138 \pm \sqrt{(1.38)^2 \times 10^{-2} - 4(1)(-0.0038)}}{2}$$

$$= 2.4 \times 10^{-2}\text{M} = [H^+]$$

Q-50 A buffer solution is prepared using oxalic acid and sodium oxalate. What must the ratio $[Ox^-]/[HOx]$ be in order that $[H^+]$ be equal to 4.5×10^{-2}M?

A-50 $$K_{eq} = \frac{[H^+][Ox^-]}{[HOx]} = 3.8 \times 10^{-2} \text{ mole/ℓ}$$

$$= \frac{(4.5 \times 10^{-2})[Ox^-]}{[HOx]}$$

$$\frac{[Ox^-]}{[HOx]} = \frac{3.8 \times 10^{-2}}{4.5 \times 10^{-2}} = 0.84$$

R a) The quantitative effect of adding a common species to an equilibrated system may be determined from the equilibrium expression.

b) A solution containing a weak acid and its salt is called a buffer. Buffer solutions resist change in $[H^+]$.

S-6 Addition of a common ion will change the position of the solubility equilibrium. Thus, addition of Cl^- will shift the following reaction to the left.

$$AgCl_{(s)} \rightleftarrows Ag^+ + Cl^-$$

If K_{sp} is known, then the quantitative aspects of the shift in equilibrium may be calculated.

Q-51 A liter of solution is saturated with AgCl. Will $[Ag^+]$ be greater, less, or the same after 1.0×10^{-4} mole of solid NaCl is added to the solution? Why? (Assume no volume change.)

A-51 Less. The product $[Ag^+][Cl^-]$ cannot exceed K_{sp}. If $[Cl^-]$ is increased by adding NaCl, then $[Ag^+]$ must decrease.

Q-52 In reference to the previous question, when 1.00×10^{-4} mole of NaCl was added to 1 liter of a saturated AgCl solution, $[Ag^+]$ decreased. What process occurred which caused the Ag^+ ion concentration to decrease?

A-52 The Ag^+ combined with Cl^- to form AgCl which precipitated from the solution.

Q-53 A solution is 0.10 M in NaCl. Excess solid AgCl is added.

(K_{sp} for AgCl = 2.8×10^{-10} mole$^2/\ell^2$)

What will $[Ag^+]$ be at equilibrium?

(Hint: What is $[Cl^-]$ at equilibrium?)

A-53 In the solution, the final Cl^- concentration will be 0.10 mole per liter (from NaCl) plus the Cl^- resulting from some AgCl dissolving. If $\underline{x}$ is the amount of Cl^- in mole/liter resulting from the dissolved AgCl, then

$$K_{sp} = [Ag^+][Cl^-] = (\underline{x})(0.10 + \underline{x})$$

Assuming $\underline{x} \ll 0.10$,

$$\underline{x}(0.10) = 2.8 \times 10^{-10} \text{ mole}^2/\ell^2$$

$$\underline{x} = 2.8 \times 10^{-9}\,M = [Ag^+]$$

Q-54 A solution is made 1.00×10^{-3} M in Ag^+ by adding enough water to 1.00×10^{-3} moles of $AgNO_3$ to make 1 liter of solution ($AgNO_3$ is very soluble in water). Will any AgCl precipitate if 1.00×10^{-4} mole of NaCl is added?

(K_{sp} for AgCl = 2.8×10^{-10} mole$^2/\ell^2$)

A-54 If the product $[Ag^+][Cl^-]$ exceeds 2.8×10^{-10} mole$^2/\ell^2$, AgCl precipitates.

$$[Ag^+] = 1.00 \times 10^{-3}\,M$$

$$[Cl^-] = 1.00 \times 10^{-4}\,M$$

The product of these two quantities (1.00×10^{-7} mole$^2/\ell^2$) is much larger than 2.8×10^{-10} mole$^2/\ell^2$. Therefore, some AgCl must precipitate until the condition

$$[Ag^+][Cl^-] = 2.8 \times 10^{-10} \text{ mole}^2/\ell^2$$

is reached.

Q-55 How many moles of AgBr

($K_{sp} = 5 \times 10^{-13}$ mole$^2/\ell^2$)

will dissolve in a 0.01 M NaBr solution? (NaBr is completely dissociated into Na^+ and Br^-.)

A-55 In the solution $[Br^-] = 0.01$ M, but the product $[Ag^+][Br^-]$ cannot exceed 5×10^{-13} mole$^2/\ell^2$

$$[Ag^+](0.01) = 5 \times 10^{-13} \text{ mole}^2/\ell^2$$

$$[Ag^+] = 5 \times 10^{-11} \text{ M}$$

Therefore, 5×10^{-11} mole of AgBr dissolved. Note that the $[Br^-]$ from dissolved AgBr is much less than the $[Br^-]$ from NaBr

Q-56 A solution is 0.010 M in Mg^{+2}. The K_{sp} of $Mg(OH)_2$ is 8.9×10^{-12} mole$^3/\ell^3$. What must the $[OH^-]$ be when $Mg(OH)_2$ just starts to precipitate?

(Hint: What is the equilibrium involved? What is the equilibrium expression? What is $[Mg^{+2}]$ when precipitation starts?)

A-56 $Mg(OH)_2 \rightleftarrows Mg^{+2} + 2OH$

$$K_{sp} = [Mg^{+2}][OH^-]^2 = 8.9 \times 10^{-12} \text{ mole}^3/\ell^3$$

$$= (0.010)[OH^-]^2 = 8.9 \times 10^{-12} \text{ mole}^3/\ell^3$$

$$[OH^-] = 3.0 \times 10^{-5} \text{ M}$$

Q-57 A solution is 0.010 M in cuprous ion (Cu^+) and 0.0010 M in lead ion (Pb^{+2}). Chloride ion is slowly added.

Will $PbCl_2$ ($K_{sp} = 1.6 \times 10^{-5}$ mole$^3/\ell^3$) or CuCl ($K_{sp} = 3.2 \times 10^{-7}$ mole$^2/\ell^2$) precipitate first? Show why

A-57 The reactions are

$$PbCl_2 \rightleftarrows Pb^{+2} + 2Cl^-$$

$$CuCl \rightleftarrows Cu^+ + Cl^-$$

Lead chloride precipitates when

$$[Pb^{+2}][Cl^-]^2 = K_{sp} = 1.6 \times 10^{-5} \text{ mole}^3/\ell^3$$

In this case,

$$[Pb^{+2}] = 0.0010 \text{ M}$$

Therefore, $PbCl_2$ precipitates when

$$[Cl^-] = \sqrt{\frac{1.6 \times 10^{-5}}{0.0010}} = 1.3 \times 10^{-1} \text{ M}$$

Cuprous chloride precipitates when

$$[Cu^+][Cl^-] = 3.2 \times 10^{-7} \text{ mole}^2/\ell^2$$

In this case,

$$[Cu^+] = 0.010 \text{ M}$$

Therefore, CuCl precipitates when

$$[Cl^-] = \frac{3.2 \times 10^{-7}}{0.010} = 3.2 \times 10^{-5} \text{ M}$$

Obviously, CuCl would precipitate first as $[Cl^-]$ of 3.2×10^{-5} M is reached before $[Cl^-]$ of 1.3×10^{-1} M.

Q-58 In the previous question, it was found that CuCl precipitates before $PbCl_2$. What will the $[Cu^+]$ be when $PbCl_2$ just starts to precipitate?

A-58 $PbCl_2$ precipitates only when $[Cl^-]$ equals 1.3×10^{-1} M. When $[Cl^-]$ is this high the $[Cu^+]$ can be calculated by

$$K_{sp} = [Cu^+][Cl^-] = 3.2 \times 10^{-7} \text{ mole}^2/\ell^2$$

$$[Cu^+] = \frac{3.2}{1.3} \times 10^{-6} = 2.5 \times 10^{-6} \text{ M}$$

[redacted]

S-7 Acids can be described as strong or weak depending upon the magnitude of the equilibrium constant. Likewise, bases can be described as being strong or weak. A strong base, such as NaOH, dissociates completely to Na^+ and OH^- (K_{eq} is very large) while a weak base, such as NH_4OH, dissociates only partially to NH_4^+ and OH^- (K_{eq} is 1.8×10^{-5} mole/ℓ)

strong base	K_{eq}-mole/ℓ	weak base	K_{eq}-mole/ℓ
NaOH	much larger than 1	NH_4OH	1.8×10^{-5}
KOH	much larger than 1	CH_3NH_3OH	5×10^{-4}
LiOH	much larger than 1	NH_2NH_3OH	9.8×10^{-7}
		$(CH_3)_3N$	5.7×10^{-5}
		$C_5H_{11}N$	1.7×10^{-3}

Q-59 A solution is prepared by dissolving 0.10 mole of NH_3 gas in enough water to make 1.0 liter of solution. What is the $[OH^-]$ in the resulting solution?

(Hint. $NH_3 + H_2O \rightarrow NH_4OH$

Therefore, the NH_4OH formed from NH_3 is 0.10 mole.

K_{eq} for the reaction $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ is 1.8×10^{-5} mole/ℓ.)

A-59 $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5} \text{ mole/ℓ}$$

Let $\underline{x} = [NH_4^+]$ formed by the dissociation of NH_4OH.

$\underline{x} = [NH_4^+] = [OH^-]$

$[NH_4OH] = 0.10 - \underline{x}$

Assuming $\underline{x} \lll 0.10$

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

$$\underline{x} = [OH^-] = 1.3 \times 10^{-3} \text{ M}$$

Q-60 One liter of a solution containing only NH_4OH and water is to have an OH^- ion concentration of 6.0×10^{-4} mole/liter. How much NH_3 gas would be required to prepare this solution?

(Hint: What is $[NH_4^+]$?)

A-60
$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5} \text{ mole/ℓ}$$

$[OH^-] = 6.0 \times 10^{-4}\text{ M} = [NH_4^+]$

$$\frac{36 \times 10^{-8}}{[NH_4OH]} = 1.8 \times 10^{-5}$$

$[NH_4OH] = 2.0 \times 10^{-2}$ M

Therefore, the original (before dissociation) concentration of NH_4OH must have been

2.0×10^{-2} mole/ℓ + 6.0×10^{-4} mole/ℓ

$= 2.1 \times 10^{-2}$ mole/ℓ.

Therefore, 2.1×10^{-2} mole NH_3 would be required.

Q-61 A solution is prepared by dissolving 0.1 mole NH_3 gas and 0.2 mole of NH_4Cl (a salt which dissociates completely into NH_4^+ and Cl^-) in enough water to form 1.0 liter of solution. What is the $[OH^-]$ in this solution?

(Hint: What is the concentration of NH_4^+ ion?)

A-61 $\underline{x}$ = $[OH^-]$ from the dissociation of NH_4OH

$[NH_4^+] = 0.2 + \underline{x}$

$[NH_4OH] = 0.1 - \underline{x}$

Assuming $\underline{x} <<< 0.1$ or 0.2,

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{0.2\,\underline{x}}{0.1} = 1.8 \times 10^{-5}\,\text{mole}/\ell$$

$\underline{x} = 9 \times 10^{-6}\,M = [OH^-]$

Q-62 If 0.001 mole OH^- ion is added to the solution given in the previous question, will $[OH^-]$ increase by 0.001 mole? Why?

A-62 $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

If more OH^- is added to the solution, the reaction given above will be shifted to the left. Such a shift will require that some OH^- ions react to form NH_4OH. Therefore, addition of 0.001 mole of OH^- ions will not increase $[OH^-]$ by 0.001 mole but something less than 0.001 mole.

Q-63 A solution of a weak base and a completely dissociated salt with a common ion (i.e., $NH_4OH + NH_4Cl$) is known as what kind of a solution?

A-63 buffer solution

Q-64 A liter of NH_4OH - NH_4Cl buffer solution was to be prepared with the $[OH^-]$ equal to 5.0×10^{-3} M. What must the $[NH_4^+]/[NH_4OH]$ ratio be in the buffer solution?

A-64 $$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}\,\text{mole}/\ell$$

$[OH^-] = 5.0 \times 10^{-3}\,M$

Therefore,

$$\frac{[NH_4^+]}{[NH_4OH]} = \frac{1.8 \times 10^{-5}}{5.0 \times 10^{-3}} = 3.6 \times 10^{-3}$$

Q-65 One liter of a buffer (pH = 5.20) is to be prepared from NH_4Cl and NH_4OH. If 0.10 mole of NH_4Cl is used, how many moles of NH_3 should be added to the solution? Assume an activity coefficient of one.

A-65 pH = 5.20

$-\log[OH^-] = 8.80$

pOH = 8.80

$[OH^-] = 1.6 \times 10^{-9}\,M$

$$K_{NH_4OH} = \frac{[OH^-][NH_4^+]}{[NH_4OH]}$$

$[OH^-] = 1.6 \times 10^{-9}\,M$

$[NH_4^+] = 0.10 + 1.6 \times 10^{-9} = 0.10\,M$

$[NH_4OH] = \underline{x}$

$$\frac{(1.6 \times 10^{-9})(0.10)}{\underline{x}} = 1.8 \times 10^{-5}\,\text{mole}/\ell$$

$\underline{x} = [NH_4OH] = 8.9 \times 10^{-6}\,M$

Add $8.9 \times 10^{-6} + 1.6 \times 10^{-9}$ mole NH_3

Weak bases dissociate only slightly and have small equilibrium constants (much less than one). Strong bases dissociate nearly completely and have large (greater than one) dissociation constants.

S-8 When salts of a strong base and a strong acid (i e , NaCl, formed from NaOH and HCl) are added to water, the hydrogen ion concentration remains unchanged However, when salts formed from strong acids and weak bases (i. e , NH_4Cl, formed from NH_4OH and HCl) or salts formed from weak acids and strong bases (i e , sodium acetate, from NaOH and HAc) are added to water, the hydrogen ion concentration changes because of a reaction between the ions of the salt and water <u>The reaction is called hydrolysis</u> In the case of NH_4Cl, the hydrolysis reactions are

$NH_4Cl \rightarrow NH_4^+ + Cl^-$ 1) complete dissociation

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$ 2) hydrolysis

$Cl^- + H_2O \rightleftharpoons HCl + OH^-$ 3) hydrolysis

Because NH_4OH is a weak base (only partially dissociated), the equilibrium for reaction (2) lies far to the right. Because HCl is completely dissociated, the equilibrium for reaction (3) lies far to the left The overall effect is that excess H^+ is formed when NH_4Cl is added to water

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Q-66 Write the hydrolysis reaction that occurs when NaCN is added to water. Will the resulting solution be acidic or basic? Why?

A-66 Basic

$NaCN \rightarrow Na^+ + CN^-$ (complete dissociation)

$Na^+ + H_2O \rightleftharpoons NaOH + H^+$

$CN^- + H_2O \rightleftharpoons HCN + OH^-$

Because HCN is a weak acid and is only slightly dissociated, the reaction of CN^- with water produces excess OH^- The reaction of Na^+ with water lies far to the left; excess H^+ is <u>not</u> formed.

Q-67 NaCl is added to water. Write the hydrolysis reaction that occurs Will the resulting solution tend to be acidic, neutral or basic? Why?

A-67 Neutral

$Na^+ + H_2O \rightleftharpoons NaOH + H^+$

$Cl^- + H_2O \rightleftharpoons HCl + OH^-$

Both NaOH and HCl are completely dissociated in aqueous solution. Both hydrolysis reactions lie far to the left, no excess H^+ or OH^- are produced so the solution remains neutral.

Q-68 NaF is added to water. Write the hydrolysis reaction. Will the resulting solution be acidic or basic?

(Hint. $K_{HF} = 6\ 9 \times 10^{-4}$ mole/ℓ)

A-68 Basic

$Na^+ + H_2O \rightleftharpoons NaOH + H^+$

Reaction lies far to the left and does not form excess H^+.

$F^- + H_2O \rightleftharpoons HF + OH^-$

HF is a weak acid so this reaction produces excess OH^-.

R When the salt of a strong acid and a weak base is dissolved in water, hydrolysis occurs to give an acidic solution. When the salt of a weak acid and a strong base is dissolved in water, hydrolysis occurs to give a basic solution.

S-9 The preceding section indicated how to qualitatively predict the effect of dissolved salts on the hydrogen ion concentration A quantitative description of a hydrolysis reaction such as

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

can be made if the equilibrium constant for the weak acid (or base) and the dissociation constant for water (K_w) are known

Q-69 Water ionizes according to the equation

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_{eq}^{25°} = 1\ 8 \times 10^{-16} \text{ mole}/\ell$$

For pure water, what is the concentration of H^+?

(Hint 1 liter of water contains 55.5 moles of H_2O)

A-69 Let $\underline{x}$ = amount of H_2O which dissociates

Then at equilibrium,

$$[H_2O] = 55\ 5 - \underline{x}$$

$$[H^+] = [OH^-] = \underline{x}$$

$$\frac{[H^+][OH^-]}{[H_2O]} = \frac{(\underline{x})(\underline{x})}{(55\ 5 - x)} = 1.80 \times 10^{-16} \text{ mole}/\ell$$

Assuming $\underline{x} << 55\ 5$,

$$\underline{x}^2 = (55.5)(1.80 \times 10^{-16})$$

$$= 1\ 00 \times 10^{-14} \text{ mole}^2/\ell^2$$

$$\underline{x} = 1\ 00 \times 10^{-7} \text{ M} = [H^+] = [OH^-]$$

Q-70 Because the number of moles of water in one liter of any aqueous solution is very nearly 55.5, a new constant K_w can be defined in the following way

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]} = 1.80 \times 10^{-16} \text{ mole}/\ell$$

$$K_w = 1\ 80 \times 10^{-16}[H_2O]$$

$$= 1.00 \times 10^{-14} \text{ mole}^2/\ell^2 = [H^+][OH^-]$$

In all aqueous solutions at 25°C, $[H^+][OH^-]$ <u>must</u> equal 1.00×10^{-14} mole²/ℓ². If a solution has a $[H^+]$ of 0.00721 M, what is $[OH^-]$ at 25°C?

A-70 $K_w = [H^+][OH^-] = 1\ 00 \times 10^{-14} \text{mole}^2/\ell^2$

$$= (0\ 00721)[OH^-]$$

$$[OH^-] = 1\ 39 \times 10^{-12} \text{ M}$$

Q-71 If an aqueous solution has an $[OH^-] = 6.2 \times 10^{-7}$ M, what is $[H^+]$ at 25°C?

A-71 $[H^+][OH^-] = 1.00 \times 10^{-14} \text{ mole}^2/\ell^2$

$$[H^+](6\ 2 \times 10^{-7}) = 1.00 \times 10^{-14}$$

$$[H^+] = 1\ 6 \times 10^{-8} \text{ M}$$

Q-72 Write the equilibrium expression (K_{hy}) for the hydrolysis reaction.

$$H_2O + Ac^- \rightleftharpoons HAc + OH^-$$

(Hint: $[H_2O]$ is constant.)

A-72 $$K_{hy} = \frac{[OH^-][HAc]}{[Ac^-]}$$

$[H_2O]$ is constant and therefore is included in the constant K_{hy}

Q-73 If the equilibrium expression for the hydrolysis of Ac^- is

$$K_{hy} = \frac{[OH^-][HAc]}{[Ac^-]},$$

express K_{hy} in terms of K_w and K_{HAc}.

$$K_w = [H^+][OH^-]$$

$$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]}$$

A-73 $$K_w = [H^+][OH^-]$$

$$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]}$$

$$\frac{[HAc]}{[Ac^-]} = \frac{[H^+]}{K_{HAc}}$$

$$K_{hy} = \frac{[OH^-][HAc]}{[Ac^-]} = \frac{[OH^-][H^+]}{K_{HAc}}$$

$$= \frac{K_W}{K_{HAc}}$$

Q-74 Consider the hydrolysis of the CN^- ion. Derive the expression for K_{hy} in terms of K_W and K_{HCN}

$$K_{hy} = \frac{[OH^-][HCN]}{[CN^-]}$$

A-74 $$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$K_{HCN} = \frac{[H^+][CN^-]}{[HCN]}$$

$$\frac{[HCN]}{[CN^-]} = \frac{[H^+]}{K_{HCN}}$$

$$K_{hy} = \frac{[HCN][OH^-]}{[CN^-]} = \frac{[H^+][OH^-]}{K_{HCN}} = \frac{K_W}{K_{HCN}}$$

Q-75 If K_{HCN} is 4.0×10^{-10} mole/ℓ, what is K_{hy} for CN^-?

A-75 Since $K_{hy} = \dfrac{K_W}{K_{HCN}}$ (derived above),

then
$$K_{hy} = \frac{1.00 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5} \text{ mole/ℓ}$$

Q-76 If K_{hy} of $CN^- = 2.5 \times 10^{-5}$ mole/ℓ, what is the $[OH^-]$ of a solution prepared from 0.10 mole of NaCN and enough water to make 500 ml of solution?

(Hint: Let $\underline{x}$ = amount of CN^- converted to HCN.)

A-76 The concentration of CN^- = 0 20 M (0 10 mole/500 ml)

$$K_{hy} = \frac{[OH^-][HCN]}{[CN^-]} = 2\ 5 \times 10^{-5} \text{ mole}/\ell$$

Let $\underline{x}$ = amount of CN^- (in mole/liter) which is converted to HCN

At equilibrium,

$$[OH^-] = \underline{x} = [HCN]$$

$$[CN^-] = 0\ 20 - \underline{x}$$

Assuming $\underline{x} << 0\ 20$, then

$$\frac{(x)(x)}{0\ 20} = 2\ 5 \times 10^{-5}$$

$$\underline{x}^2 = 5\ 0 \times 10^{-6} \text{ mole}^2/\ell^2$$

$$\underline{x} = 2\ 2 \times 10^{-3} \text{ M} = [OH^-]$$

Q-77 Considering the answer to the previous problem, what would the $[H^+]$ be in a 0 20 molar NaCN solution?

A-77 In a 0 2 M NaCN solution,

$$[OH^-] = 2\ 2 \times 10^{-3} \text{ M}$$

$$[H^+][OH^-] = 1.00 \times 10^{-14} \text{ mole}^2/\ell^2$$

$$[H^+] = \frac{1\ 00 \times 10^{-14}}{2\ 2 \times 10^{-3}}$$

$$= 4\ 5 \times 10^{-12} \text{ M}$$

Q-78 Sodium fluoride is the salt of the weak acid HF(K_{diss} = 6 9 x 10^{-4} mole/ℓ) What is K_{hy} for the F^- ion?

(Hint Write the hydrolysis equation and then derive K_{hy} in terms of other constants)

A-78 $F^- + H_2O \rightleftarrows HF + OH^-$

$$K_{hy} = \frac{[HF][OH^-]}{[F^-]}$$

$$K_{HF} = \frac{[H^+][F^-]}{[HF]}$$

$$\frac{[HF]}{[F^-]} = \frac{[H^+]}{K_{HF}}$$

$$K_{hy} = \frac{[H^+][OH^-]}{K_{HF}} = \frac{K_w}{K_{HF}}$$

$$K_{hy} = \frac{1\ 00 \times 10^{-14}}{6.9 \times 10^{-4}} = 1\ 4 \times 10^{-11} \text{ mole}/\ell$$

Q-79 If K_{hy} for F^- is 1.4 x 10^{-11} mole/ℓ, what is $[H^+]$ in a solution prepared by dissolving 0 10 mole of NaF in enough water to make 500 ml of solution?

A-79 Let $[HF] = \underline{x}$

$$[OH^-] = \underline{x}$$

$$[F^-] = 0.20 - \underline{x}$$

Assuming $\underline{x} << 0.20$

$$K_{hy} = \frac{(x)(x)}{0.20} = 1\ 5 \times 10^{-11} \text{ mole}/\ell$$

$$\underline{x}^2 = 2.8 \times 10^{-12}$$

$$\underline{x} = 1.7 \times 10^{-6} \text{ M} = [OH^-]$$

$$[OH^-][H^+] = 1.00 \times 10^{-14} \text{ mole}^2/\ell^2$$

$$[H^+] = 5\ 9 \times 10^{-9}$$

Q-80 Calculate the pH of a solution prepared by mixing 0.10 mole of sodium acetate with enough water to make 1.0 liter of solution

$$K_{HAc} = 1.9 \times 10^{-5} \text{ mole}/\ell$$

Assume an activity coefficient of one.

A-80 $K_{hy} = \frac{K_W}{K_{HAc}} = \frac{[HAc][OH^-]}{[Ac^-]}$

If $\underline{x}$ equals the amount of HAc formed, then,

$[HAc] = \underline{x}$

$[OH^-] = \underline{x}$

$[Ac^-] = 0\ 10 - \underline{x}$

Assuming $\underline{x} << 0\ 10$

$$\frac{x^2}{0\ 10} = \frac{10^{-14}}{1\ 9 \times 10^{-5}}$$

$\underline{x}^2 = 5\ 3 \times 10^{-11}$ mole$^2/\ell^2$

$\underline{x} = 7\ 3 \times 10^{-6}$ M

pOH = 5 14

pH = 14 00 - 5 14 = 8 86

Q-81 Calculate the pH of a solution prepared by mixing 0 50 mole of ammonium chloride with enough water to make 1 liter of solution

$K_{NH_4OH} = 1\ 8 \times 10^{-5}$ mole/ℓ

Assume an activity coefficient of one

A-81 $K_{hy} = \frac{K_W}{K_{NH_4OH}} = \frac{[NH_4OH][H^+]}{[NH_4^+]}$

If $\underline{x}$ equals the amount of NH_4OH formed, then

$[NH_4OH] = \underline{x}$

$[H^+] = \underline{x}$

$[NH_4^+] = 0\ 50 - \underline{x}$

Assuming $\underline{x} << 0.50$

$$\frac{x^2}{0\ 50} = \frac{10^{-14}}{1\ 8 \times 10^{-5}}$$

$\underline{x} = 1.7 \times 10^{-5}$ M

pH = 4.77

R **When salts of weak acids and strong bases or salts of weak bases and strong acids dissolve in water, hydrolysis occurs.**

$$K_{hy} = \frac{K_W}{K_{\text{dissociation of acid or base}}}$$

PART III: Acid-Base Titrations

S-1 The progressive addition of an acid to a base, or vice-versa, is called titration When a solution of acid is titrated with a base, the reaction

$$H^+ + OH^- \rightleftharpoons H_2O$$

occurs. At the equivalence point, the moles of base added is exactly equal to the moles of H^+ ion in the original solution. During the titration, $[H^+][OH^-]$ will always equal 1.00×10^{-14} mole$^2/\ell^2$ at 25°.

Q-1 A 50 00 ml sample of 0 1000 M HCl is titrated with 0 1000 M NaOH, i e , the NaOH is progressively added to the HCl What is the pH at

a) the start of the titration,

b) after 25 00 ml of NaOH has been added,

c) after 49 90 ml of NaOH have been added?

Assume an activity coefficient of 1.

A-1 a) at the start of the titration,

$[H^+] = 0\ 1\ M$ (pH = 1)

b) $\dfrac{50\ 00\ \cancel{ml\ HCl}}{} \Big| \dfrac{0\ 1000\ mole\ HCl}{1000\ \cancel{ml\ HCl}} = 5.000 \times 10^{-3}$ mole HCl initially present

$\dfrac{25.00\ \cancel{ml\ NaOH}}{} \Big| \dfrac{0\ 1000\ mole\ NaOH}{1000\ \cancel{ml\ NaOH}} = 2.500 \times 10^{-3}$ mole NaOH added

This added NaOH combines with 2.500×10^{-3} mole of HCl to form $2\ 500 \times 10^{-3}$ mole NaCl Therefore, $2\ 500 \times 10^{-3}$ mole of HCl are left in 75.00 ml of solution

$$[H^+] = \frac{2\ 500 \times 10^{-3}\ mole\ H^+}{75\ 00\ \cancel{ml}} \Big| \frac{1000\ \cancel{ml}}{1\ liter} = 0.033\ M$$

pH = 1 48

c) $\dfrac{49\ 90\ \cancel{ml\ NaOH}}{} \Big| \dfrac{0\ 1000\ \cancel{mole\ NaOH}}{1000\ \cancel{ml\ NaOH}} \Big| \dfrac{1\ mole\ HCl}{1\ \cancel{mole\ NaOH}} = 4.990 \times 10^{-3}$ mole HCl

49.90 ml of NaOH combines with 4.990×10^{-3} mole of HCl. The moles of HCl remaining are

$5\ 000 \times 10^{-3} - 4.990 \times 10^{-3} = 1.0 \times 10^{-5}$ mole.

$$[H^+] = \frac{1.0 \times 10^{-5}\ mole\ H^+}{99.9\ \cancel{ml}} \Big| \frac{1000\ \cancel{ml}}{1\ liter} = 1.0 \times 10^{-4}\ M$$

pH = 4

Q-2 For the titration described in the preceding question, what will the pH be when

a) 50.00 ml of NaOH solution is added,

b) 50.10 ml of NaOH solution is added, and

c) 60.00 ml of NaOH solution is added?

A-2 a) When 50 00 ml of NaOH is added, the equivalence point (moles of base added equal moles of acid in sample) will be reached. Because NaCl (the product formed) is the salt of a strong acid and strong base, the solution will be neutral

pH = pOH = 7

b) When 50 10 ml of NaOH solution has been added, the excess NaOH will be

$$\frac{0\ 10\ \cancel{\text{ml}}\ \big|\ 0\ 1000\ \text{mole NaOH}}{1000\ \cancel{\text{ml NaOH}}} = 1\ 0 \times 10^{-5}\ \text{mole in } 100\ 1\ \text{ml}$$

$[OH^-]$ = 1.0×10^{-4} M

pOH = 4

pH = 10

c) When 60 00 ml of NaOH solution has been added, the excess NaOH will be

$$\frac{(10\ 00)(0\ 1000)}{1000}\ \text{mole NaOH in 110 ml}$$

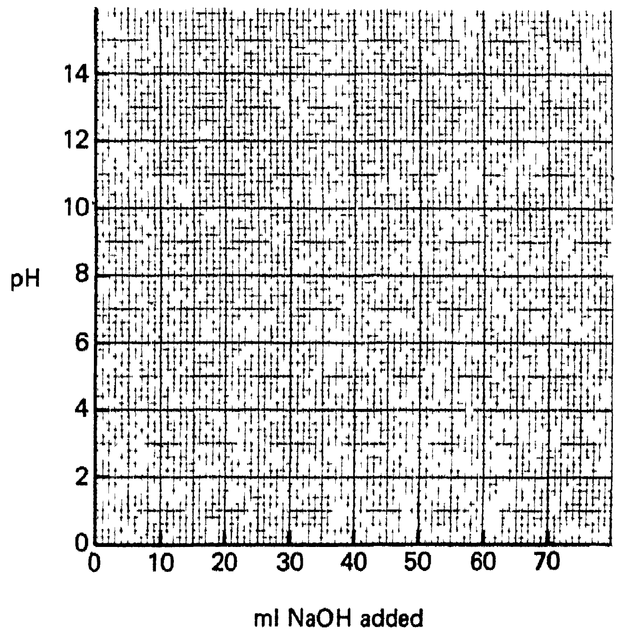
$$[OH^-] = \frac{(1 \times 10^{-3})(1000)}{110}\ \text{mole/liter}$$

$[OH^-]$ = 9.1×10^{-3} M

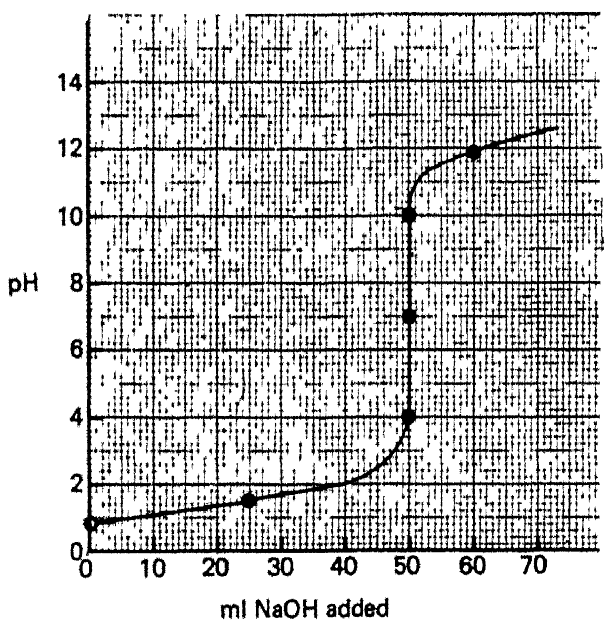
pOH = 2.04

pH = 11.96

Q-3 Using the data calculated in the two preceding problems, draw a titration curve by plotting ml of NaOH added (X-axis) against pH (Y-axis).



A-3



Q-4 The equivalence point in the titration of a strong acid with a strong base is always at pH 7 Why?

A-4 The salt formed by such a titration will always be completely dissociated. No hydrolysis occurs with salts formed from strong acids and strong bases.

Q-5 The equivalence point in the titration of a weak acid with a strong base is <u>not</u> at pH 7. A solution of acetic acid is titrated to the equivalence point with NaOH. What is the salt formed? Will the pH of the solution be greater than or less than 7? Why?

A-5 The salt formed is sodium acetate

$$HAc + NaOH \rightarrow H_2O + NaAc$$

The pH of the solution will be greater than 7 because of hydrolysis

$$Ac^- + H_2O \rightleftarrows HAc + OH^-$$

Q-6 A solution of HCN is titrated to the equivalence point with NaOH Give the titration reaction Will the pH of the resulting solution be greater or less than 7? Why?

A-6 $HCN + NaOH \rightarrow NaCN + H_2O$

The pH will be greater than 7 because of hydrolysis

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

Q-7 A solution of NH_4OH is titrated to the equivalence point with HCl What is the salt formed? Will the pH of the resulting solution be equal to, greater than, or less than 7? Why?

A-7 The salt formed is NH_4Cl

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

The pH will be less than 7 because of hydrolysis

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Q-8 A 50 00 ml sample of 0 100 M acetic acid (K_{HAc} 1 9 x 10^{-5} mole liter) is titrated with 0 100 M NaOH Before titration, the pH of the acetic acid solution is 2 9 Calculate the pH of the solution after 40 ml, 50 ml, and 60 ml of 0.10 M NaOH is added. (Assume activity coefficient is equal to one)

A-8 a) $\dfrac{50 \cancel{\text{ml HAc}}}{} \left| \dfrac{0.100 \text{ mole HAc}}{1000 \cancel{\text{ml HAc}}} \right. = 5\ 0 \times 10^{-3}$ mole of HAc initially present

$\dfrac{40 \cancel{\text{ml NaOH}}}{} \left| \dfrac{0\ 100 \text{ mole NaOH}}{1000 \cancel{\text{ml NaOH}}} \right. = 4.0 \times 10^{-3}$ mole NaOH added

This added NaOH combines with $4\ 0 \times 10^{-3}$ mole of HAc to form $4\ 0 \times 10^{-3}$ mole of NaAc

Therefore, 1.0×10^{-3} mole of HAc are left in 90 ml of solution.

$$[HAc] = \frac{1\ 0 \times 10^{-3} \text{ mole HAc}}{90 \cancel{\text{ml}}} \left| \frac{1000 \cancel{\text{ml}}}{1 \text{ liter}} \right. = 0.011 \text{ M}$$

$$[Ac^-] = \frac{4.0 \times 10^{-3} \text{ mole NaAc}}{90 \cancel{\text{ml}}} \left| \frac{1000 \cancel{\text{ml}}}{1 \text{ liter}} \right. = 0.044 \text{ M}$$

$$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]}$$

let $\underline{x} = [H^+]$

$[Ac^-] = 0.044 + \underline{x}$

$[HAc] = 0.011 - \underline{x}$

assuming $\underline{x} << 0\ 011$

$$\underline{x} = \frac{(1.9 \times 10^{-5})(0\ 011)}{(0\ 044)} = 4.8 \times 10^{-6} \text{ M}$$

pH = 5 32

b) 50 ml

Since at the equivalent point the moles of NaOH are just equal to the moles of HAc, the solution contains 5.0×10^{-3} moles of NaAc.

$$[NaAc] = \frac{5.0 \times 10^{-3} \text{ mole NaAc}}{100 \cancel{\text{ml}}} \left| \frac{1000 \cancel{\text{ml}}}{1 \text{ liter}} \right. = 0.050 \text{ M}$$

The hydrolysis reaction is

$$Ac^- + H_2O \rightleftarrows HAc + OH^-$$

$$K_{hy} = \frac{K_{water}}{K_{HAc}} = \frac{[OH^-][HAc]}{[Ac^-]} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-5}} = 5.3 \times 10^{-10} \text{ mole}/\ell$$

let $[OH^-] = \underline{x} = [HAc]$

$[Ac^-] = 0.050$ M

$$\frac{\underline{x}^2}{0.050} = 5.3 \times 10^{-10}$$

$\underline{x}^2 = 2.6 \times 10^{-11}$ mole$^2/\ell^2$

$\underline{x} = 5.1 \times 10^{-6}$ mole$/\ell$

pOH = 5.29

pH = 8.71

c) $$\frac{60 \cancel{\text{ ml NaOH}} \mid 0.100 \text{ mole NaOH}}{\mid 1000 \cancel{\text{ ml NaOH}}} = 6.0 \times 10^{-3} \text{ mole NaOH added}$$

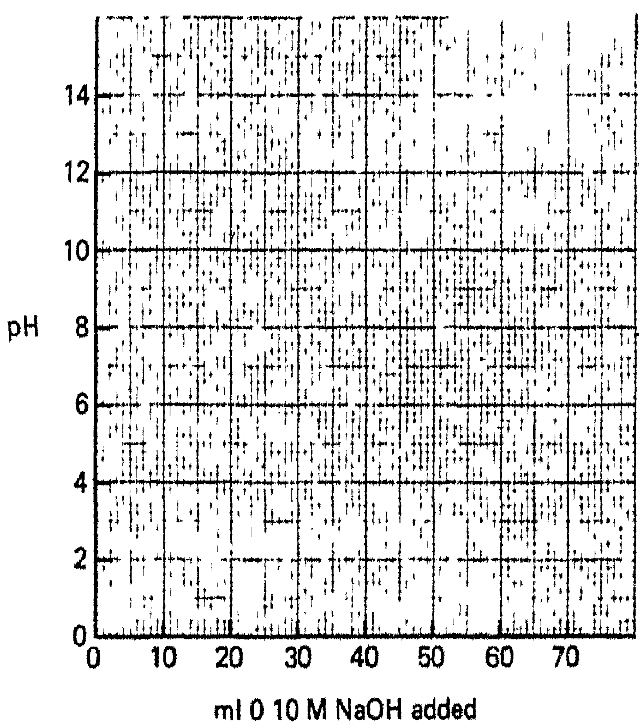
50 ml of NaOH is used to neutralize the HAc present. Therefore, 1.0×10^{-3} mole of NaOH remain unreacted.

$$[OH^-] = \frac{1.0 \times 10^{-3} \text{ mole NaOH} \mid 1000 \text{ ml}}{110 \text{ ml} \mid 1.0\ \ell} = 9.1 \times 10^{-3} \text{ M}$$

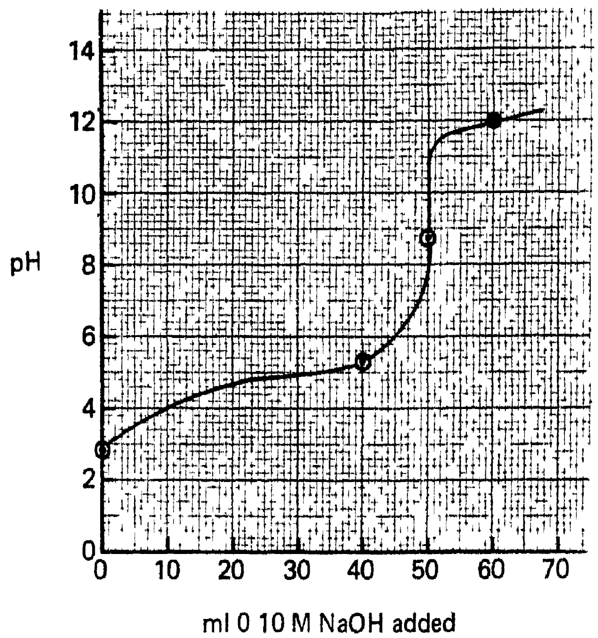
pOH = 2.04

pH = 14.00 - 2.04 = 11.96

Q-9 Using the pH values calculated in A-8, draw the titration curve for the titration of 50 ml of 0.10 M HAc with a 0.10 M solution of NaOH.



A-9



R In the titration of an acid with a base (or vice-versa), the pH changes very rapidly at the equivalence point The equivalence point in the titration of a strong acid with strong base is at pH 7 In the titration of weak acids with strong bases (or vice-versa), the equivalence point is not at pH 7 because of the hydrolysis of the salt formed in the titration reaction

S-2 Indicators are used to detect equivalence points in an acid-base titration Indicators, such as HIn, are organic acids which can dissociate according to the following equation.

$$HIn \rightleftarrows H^+ + In^-$$

The equilibrium expression for the indicator HIn is

$$K_{eq} = \frac{[H^+][In^-]}{[HIn]}$$

The ratio $[In^-]/[HIn]$ is inversely proportional to $[H^+]$.

Q-10 For the indicator HIn, the species In^- is colorless and the species HIn is red If the indicator is added to a strongly acidic solution, which species, HIn or In^-, will be present in the larger amount? Why?

A-10 HIn In an acid solution, the equilibrium for the reaction

$$HIn \rightleftarrows H^+ + In^-$$

will lie far to the left.

Q-11 If HIn is the predominate species in a solution, will the solution appear red or colorless?

A-11 Red

Q-12 For the indicator HIn,

$$K_{eq} = 5 \times 10^{-6} \text{ mole/liter}$$

When the ratio, $[In^-]/[HIn]$, is $\frac{1}{2}$ or less, the eye can detect a red color in the solution What is the pH of a solution containing HIn when the eye can just detect a red color?

A-12 $K = \dfrac{[H^+][In^-]}{[HIn]}$

$\dfrac{[H^+]}{2} = 5 \times 10^{-6}$ mole/ℓ

$[H^+] = 1.0 \times 10^{-5}$ M

pH = 5

Q-13 For an indicator HIn'

$K_{eq} = 5 \times 10^{-10}$ mole/liter

When the ratio, $[In'^-]/[HIn']$, is 1/10 or less, the eye can detect a blue color What is the highest pH at which a solution of HIn' appears blue?

A-13 $K = \dfrac{[H^+][In'^-]}{[HIn']}$

$\dfrac{[H^+]}{10} = 5 \times 10^{-10}$ mole/ℓ

$[H^+] = 5 \times 10^{-9}$ M

pH = 8 3

Q-14 For the indicator HIn'', the ratio $[In''^-]/[HIn'']$ is 7 0 at a pH of 4.3 What is K_{eq} for the indicator?

A-14 pH = 4 3

$-\log[H^+] = 4\ 3$

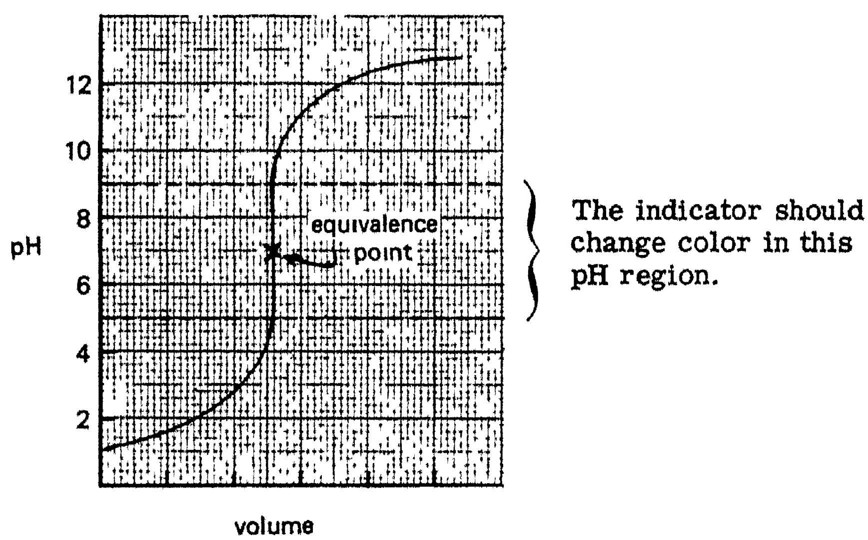
$[H^+] = 5.0 \times 10^{-5}$ M

$K_{eq} = \dfrac{[H^+][In''^-]}{[HIn'']}$

$= (5.0 \times 10^{-5})(7.0)$

$= 3.5 \times 10^{-4}$ mole/ℓ

S-3 Indicators for a particular titration are chosen so that a visual color change will occur at or very near the pH of the solution at the equivalence point



Q-15 The indicator methyl red is red in acid solution and yellow in basic solution. The color transformation can be detected with the eye at pH 5. Would this be a suitable indicator for the titration described in S-3?

A-15 Yes. Any indicator changing in the pH range 5 to 9 would be acceptable

Q-16 The color transformation for the indicator methyl orange (red in acid, yellow in base) can be detected at pH 4. Would methyl orange be a suitable indicator for the titration described in S-3?

A-16 No The color transformation of methyl orange occurs at too low a pH.

Q-17 An acid is titrated with a base (base is added to the acid solution containing the indicator) The titration curve is identical to that given in S-3 If methyl orange is used as indicator would the color change be detected before or after the equivalence point has been reached?

A-17 Before the equivalence point has been reached

Q-18 Figure I is a titration curve for the titration of a base with an acid (acid added to the base containing indicator) Figure II shows an expanded portion of the curve in Figure I. If a titration of this acid and base were carried out, describe the type of error and magnitude of error (in terms of ml of acid added) for the indicators x and y

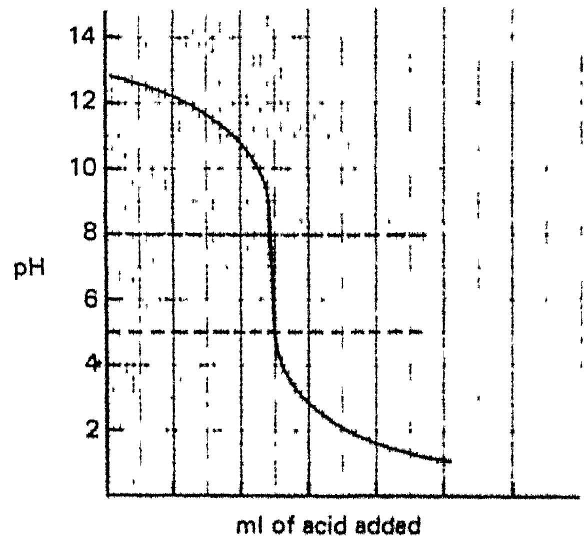


Figure I

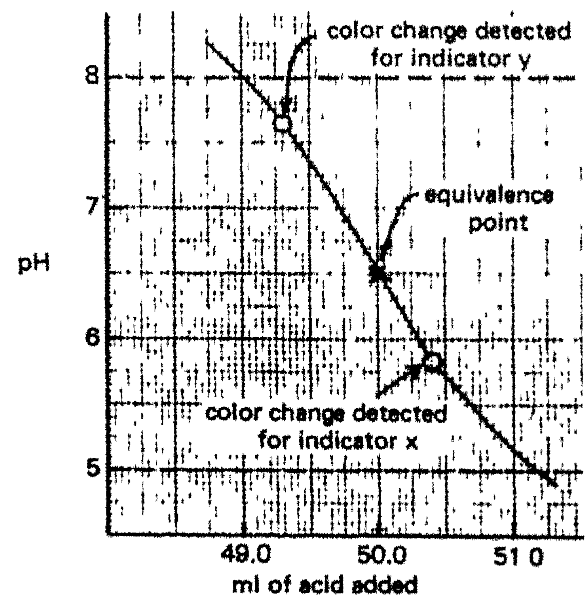


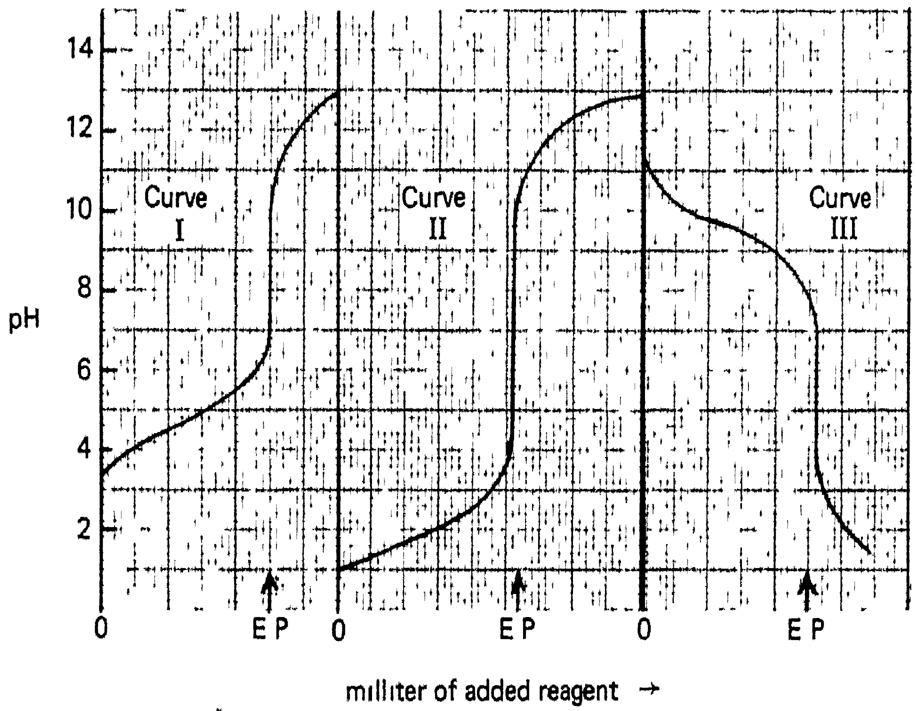
Figure II

A-18 For indicator y, 0 7 ml too little acid would be added For indicator x, 0 4 ml too much acid would be added

Q-19 For the titration described in Q-18, which indicator would give the most accurate result?

A-19 Indicator x

Q-20 A weak acid is titrated with a strong base (base is added to the acid and indicator) Which curve would most closely represent the pH changes during this titration? Why?



A-20 Curve I. At the equivalence point, the solution will be slightly basic. Salts of weak acids and strong bases give basic solution because of hydrolysis.

Q-21 Which of the curves given in Q-20 would most closely represent the titration of a weak base with a strong acid? Why?

A-21 Curve III. At the equivalence point, the solution would be slightly acidic. Salts of weak bases and strong acids give acidic solutions because of hydrolysis.

Q-22 Thymolphthalein is an indicator which changes color in the pH range 9-11 Would this indicator be satisfactory for the titration described by curve I in Q-20? Why?

A-22 Yes, the equivalence point for curve I comes at about pH 9. If thymolphthalein were used, the color change would occur very close to the equivalence point.

Q-23 Methyl orange changes color in the pH range 3-4, while methyl red changes color in the pH range 5-6. Which would be the most satisfactory indicator for the titration described by curve III in Q-20? Why?

A-23 Methyl red The equivalence point on curve III comes at about pH 5 The color change with methyl red would occur very close to the equivalence point If methyl orange were used, the color change would occur after the equivalence point is reached

Q-24 A 50 00 ml sample of 0 100 molar acetic acid (K_{eq} = 1 9 x 10^{-5} mole/ℓ) is titrated with 0 100 molar NaOH What is the best indicator to use in the titration?

Indicator	pH range of color change
Methyl orange	3-4
Methyl red	5-6
Bromthymol Blue	6-7.5
Phenolphthalein	8-9.5
Thymolphthalein	9-11

A-24 Phenolphthalein At the equivalence point the concentration of sodium acetate is 0 0500 mole/liter (100 ml of solution)

$$K_{hy} = \frac{K_w}{K_{diss}} = \frac{[HAc][OH^-]}{[Ac^-]}$$

Let $\underline{x}$ = $[OH^-]$ = $[HAc]$

$$(\underline{x})^2 = \frac{(0\ 0500)(1\ 00 \times 10^{-14})}{(1\ 9 \times 10^{-5})} \text{mole}^2/\ell^2$$

$$(\underline{x}) = 5\ 1 \times 10^{-6}\ M = [OH^-]$$

pH = 8 71

Q-25 A 50 00 ml sample of 0 100 molar NH_4OH (K_{eq} = 1 8 x 10^{-5} mole/ℓ) is titrated with 0 100 molar HCl Which of the indicators listed in Q-24 would be best for this titration?

A-25 Methyl red At the equivalence point the concentration of NH_4Cl is 0 0500 mole/liter

$$K_{hy} = \frac{K_w}{K_{diss}} = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

Let $\underline{x}$ = $[H^+]$ = $[NH_4OH]$

$$(\underline{x})^2 = \frac{(0\ 0500)(1\ 00 \times 10^{-14})}{(1\ 8 \times 10^{-5})}$$

$$\underline{x} = 5\ 3 \times 10^{-6}\ M = [H^+]$$

pH = 5 28

R For an acid-base titration, an indicator should be selected which changes color at a pH which corresponds, as closely as possible, to the pH of the equivalence point.

PART IV: Complex Ions

S-1 Certain metal ions react with electron donating groups to form complex ions. For example,

$$Cu^+ + 2CN^- \rightleftharpoons \underset{\text{complex ion}}{Cu(CN)_2^-}$$

Usually, equilibrium expressions are written and constants are given for the dissociation of the complex ion Thus, K_d for $Cu(CN)_2^-$ is expressed as

$$K_d = \frac{[Cu^+][CN^-]^2}{[Cu(CN)_2^-]} = \cdot 1 \times 10^{-16}\ \text{mole}^2/\ell^2$$

If K_d values are available, the concentrations of complex ions in solutions can be calculated.

Q-1 If one liter of a solution is 1 00 M in CN^- and 0 010 mole of copper (I) ion is added, will the final Cu^+ concentration in the solution be approximately 0 010 M, slightly less than 0 010 M or very much less than 0 010 M? Why?

(K_d for $Cu(CN)_2^-$ = 1×10^{-16} mole$^2/\ell^2$)

A-1 Because of the very small equilibrium constant (1×10^{-16} mole$^2/\ell^2$) very little of the complex dissociates The concentration of CN^- is more than twice as large as the Cu^+ concentration, therefore, virtually all of the Cu^+ will be converted to $Cu(CN)_2^-$ and the final $[Cu^+]$ will be very small - much, much less than 0 010 M

Q-2 For the solution described in the previous question, what will be the approximate final $[CN^-]$?

A-2 If nearly all Cu^+ is converted to $Cu(CN)_2^-$, then CN^- corsumed in this reaction will be nearly 0 020 M This leaves a final $[CN^-]$ of about $1.00 - 0.020 = 0.98$ M

Q-3 For the solution described in Q-1, what will be the approximate final concentration of $Cu(CN)_2^-$?

A-3 If nearly all the Cu^+ is converted to $Cu(CN)_2^-$, the final concentration of the complex will be very nearly 0.010 M

Q-4 Keeping in mind the approximations noted in the last three answers, what is the final concentration of Cu^+?

(Hint $K_d = \dfrac{[Cu^+][CN^-]^2}{[Cu(CN)_2^-]}$)

A-4 Using the previous approximations,

$$\frac{[Cu^+](0\ 98)^2}{0.01} = 1 \times 10^{-16} \text{ mole}^2/\ell^2$$

$[Cu^+] = 1 \times 10^{-18}$ M

Note that all approximations were justified.

Q-5 One liter of a solution contains 0 020 mole of CN^-, 0 010 mole of copper (I) ion is added to this solution. What will the approximate final concentrations of $Cu(CN)_2^-$, CN^-, and Cu^+ be?

$K_d = 1.0 \times 10^{-16}$ mole$^2/\ell^2$

A-5 Because of the very small K_d, nearly all the Cu^+ will be in the form of cyanide complex. Therefore, $[Cu^+]$ will be very much smaller than 0.010 M and $[Cu(CN)_2^-]$ will be very nearly 0.010 M. If 0.010 M of Cu^+ is converted to $Cu(CN)_2^-$, 0.020 M of CN^- is required; therefore, $[CN^-]$ must be nearly zero.

Q-6 For the solution described in the previous question, calculate the <u>actual</u> final concentration of Cu^+ using the approximations given in A-5.

(Hint· Let $\underline{x} = [Cu^+]$ at equilibrium; $[CN^-]$ will be $2\underline{x}$ Why?)

A-6 Let $\underline{x}$ = $[Cu^+]$, then $[CN^-]$ = $2\underline{x}$
Because the CN^- was available in the stoichiometric amount, $[Cu(CN)_2^-]$ will be approximately 0 010 M

$$\frac{[Cu^+][CN^-]^2}{[Cu(CN)_2^-]} = \frac{(\underline{x})(2\underline{x})^2}{0\ 010} = 1\ 0 \times 10^{-16}\ \text{mole}^2/\ell^2$$

$4\underline{x}^3 = 1\ 0 \times 10^{-18}\ \text{mole}^3/\ell^3$

$\underline{x} = 6\ 3 \times 10^{-7}\ M = [Cu^+]$

Q-7 Cuprous chloride has a K_{sp} of $3\ 2 \times 10^{-7}\ \text{mole}^2/\ell^2$ In the preceding question, the final $[Cu^+]$ was $6\ 3 \times 10^{-7}$ M How many moles of Cl^- would have to be added to that solution before CuCl precipitated?

(Hint Remember that the solubility product must be satisfied in any solution)

A-7 In A-6, $[Cu^+] = 6\ 3 \times 10^{-7}$ M Whenever $[Cu^+][Cl^-]$ becomes larger than $3\ 2 \times 10^{-7}$, precipitation of CuCl will occur

$[Cu^+][Cl^-] = 3\ 2 \times 10^{-7}$

$(6\ 3 \times 10^{-7})[Cl^-] = 3\ 2 \times 10^{-7}$

$[Cl^-] = 0\ 51$ M

Precipitation occurs only when $[Cl^-] = 0\ 51$ M or larger

Q-8 A 0 20 mole sample of CuCl is added to 1 0 liter of water How much KCN must be added in order to bring all the CuCl into solution? Assume no volume change on addition of the solids.

(Hint What is the maximum $[Cu^+]$ possible in solution? What will the approximate concentration of $Cu(CN)_2^-$ be when all the CuCl has dissolved?)

K_d for $Cu(CN)_2^- = 1\ 0 \times 10^{-16}\ \text{mole}^2/\ell^2$

A-8 The maximum possible concentration of Cu^+ can be calculated from K_{sp} of CuCl

$[Cu^+][Cl^-] = 3\ 2 \times 10^{-7}\ \text{mole}^2/\ell^2$

$[Cu^+] = 5.6 \times 10^{-4}$ M

When all the CuCl has dissolved, $[Cu(CN)_2^-]$ must be $0\ 20 - 5\ 6 \times 10^{-4}$ or approximately 0.20 mole per liter.

$$K_d = \frac{[Cu^+][CN^-]^2}{[Cu(CN)_2^-]} = \frac{5\ 6 \times 10^{-4}[CN^-]^2}{0.20} = 1\ 0 \times 10^{-16}\ \text{mole}^2/\ell^2$$

$[CN^-] = 1\ 9 \times 10^{-7}$ M

Q-9 Mercuric ion forms a complex with chloride ion

$HgCl_4^{-2} \rightleftharpoons Hg^{+2} + 4Cl^-$

$K_d = 1\ 0 \times 10^{-16}\ \text{mole}^4/\ell^4$.

If a solution is prepared by adding 0.010 mole of $Hg(NO_3)_2$ (a soluble salt which dissociates completely) and 0.10 mole of KCl to a liter of water, what will be the approximate concentrations of Cl^-, Hg^{+2}, and $HgCl_4^{-2}$ at equilibrium? (Assume no volume change

A-9 Because of the small K_d, very little $HgCl_4^{-2}$ dissociates, therefore, $HgCl_4^{-2}$ will be very close to 0 010 M The Hg^{+2} on the other hand, must be <u>very</u> small (much, much smaller than 0 010 M) For every mole of Hg^{+2} converted to $HgCl_4^{-2}$, 4 moles of Cl^- are required So if $[HgCl_4^{-2}]$ is close to 0 010 M, then 0 040 mole of Cl^- must have been converted, making final $[Cl^-]$ = 0 10 - 0.040 = 0 06 M

Q-10 Remembering the approximations made in the preceding answer, calculate the final concentration of Hg^{+2} in the solution described in the previous question

A-10 The approximations made were

$$[Cl^-] = 0\ 06\ M$$

$$[HgCl_4^{-2}] = 0\ 010\ M$$

$$K_d = \frac{[Hg^{+2}]\,[Cl^-]^4}{[HgCl_4^{-2}]} = 1\ 0 \times 10^{-16}\, mole^4/\ell^4$$

$$= \frac{[Hg^{+2}]\,(0\ 06)^4}{(0\ 010)} = 1\ 0 \times 10^{-16}$$

$$[Hg^{+2}] = \frac{1\ 0 \times 10^{-18}}{(0\ 06)^4} = 8 \times 10^{-14}\ M$$

Q-11 Considering the answer to the preceding question, will the final Cl^- concentration in this solution be nearly the same as approximated?

A-11 $[Cl^-] = 0.10 - 4[HgCl_4^{-2}]$

$[HgCl_4^{-2}] = 0.010 - 8 \times 10^{-14} = 0\ 010$ M

Thus,

$[Cl^-] = 0\ 10 - 4(0.010) = 0\ 06$ M

which is the same as the original approximation.

Q-12 A solution is prepared by adding 0 10 mole of $Hg(NO_3)_2$ and 0.10 mole of KCl to one liter of water Assuming no volume change, what will be the final concentration of Hg^{+2}?

(Hint What is the limiting reagent? What approximations can be made?)

A-12 Four moles of Cl^- per mole of Hg^{+2} are required to form $HgCl_4^{-2}$. In the problem described, only one mole of Cl^- per mole of Hg^{+2} is present, therefore, the Cl^- will limit $[HgCl_4^{-2}]$. The maximum value of $[HgCl_4^{-2}]$ will be

$$\frac{0.10}{4} = 0\ 025\ M$$

From the K_d value of $HgCl_4^{-2}$, it can justifiable be assumed that $[HgCl_4^{-2}]$ will be very close to its maximum value of 0.025 mole/liter, and that $[Cl^-]$ will be <u>very</u> small - much, much smaller than 0.10 M. If only 0.025 mole of $HgCl_4^{-2}$ is formed, then $[Hg^{+2}]$ left in solution must be

$$0.10 - 0.025 = 0\ 08\ M$$

Q-13 Calculate the concentration of Hg^{+2} and Cl^- remaining in the solution described in the preceding question

(Hint: Let <u>x</u> = concentration of Cl^- in the final solution.)

A-13 Cl^- is the limiting ion

Let $\underline{x}$ = final $[Cl^-]$

Final $[Hg^{+2}] = 0\ 10 - [HgCl_4^{-2}]$

$$[HgCl_4^{-2}] = \frac{(0\ 10 - \underline{x})}{4}$$

Therefore,

$$[Hg^{+2}] = 0\ 10 - \frac{(0\ 10 - \underline{x})}{4} = 0\ 08 + \frac{\underline{x}}{4}$$

$$K_d = \frac{[Hg^{+2}][Cl^-]^4}{[HgCl_4^{-2}]}$$

Making the approximations (as in the preceding answer) that

$[Hg^{+2}] = 0\ 08$ M and

$[HgCl_4^{-2}] = 0\ 025$ M

the following equation results

$$\frac{(0\ 08)(\underline{x})^4}{0\ 025} = 1 \times 10^{-16}\ mole^4/\ell^4$$

$\underline{x}^4 = 0\ 3 \times 10^{-16} = 3000 \times 10^{-20}\ mole^4/\ell^4$

$\underline{x} = 7 \times 10^{-5}$ M

$[Cl^-]_{final} = 7 \times 10^{-5}$ M

$$[Hg^{+2}]_{final} = 0\ 08 + \frac{7 \times 10^{-5}}{4}$$

$= 0\ 08 + 0\ 00002 = 0.08$ M

Q-14 Silver ion, Ag^+, forms a complex with NH_3

$Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2NH_3$

$K_d = 6 \times 10^{-8}\ mole^2/\ell^2$

If 0 010 mole of $AgNO_3$ (a soluble salt) is added to one liter of 0 10 M NH_4OH, what will be the approximate concentration of NH_3 (NH_4OH), Ag^+, and $Ag(NH_3)_2^+$ at equilibrium?

(Hint What is the limiting reagent?)

A-14 From the K_d value, it may be assumed that little $Ag(NH_3)_2^+$ will dissociate. Because the limiting reagent is Ag^+, it can be approximated that $[Ag^+]_{(final)}$ will be very small - much, much smaller than 0.010 M, and that $[Ag(NH_3)_2^+]_{(final)}$ will be nearly 0.010 M. The concentration of NH_3 will be reduced by 0 010 x 2 mole/liter or

$[NH_4OH]_{final} = 0.10 - 0\ 02 = 0\ 08$ M

Q-15 Using the approximations made in the preceding answer, calculate the final concentration of Ag^+ in the solution described in the previous question.

A-15

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6 \times 10^{-8}\ mole^2/\ell^2$$

Approximating

$[Ag(NH_3)_2^+] = 0.010$ M

$[NH_3] = 0.08$ M

Then,

$$\frac{[Ag^+](0.08)^2}{(0.010)} = 6 \times 10^{-8}$$

$[Ag^+] = 9.4 \times 10^{-8}$ M

Note that the assumptions were justified.

Q-16 An excess of solid AgCl is added to one liter of 0.1 M NH_4OH.

K_d for $Ag(NH_3)_2^+ = 6 \times 10^{-8}\ mole^2/\ell^2$

K_{sp} for AgCl $= 2.8 \times 10^{-10}\ mole^2/\ell^2$

Assuming no volume change, what will be the product of $[Ag^+][Cl^-]$?

A-16 $K_{sp} = [Ag^+][Cl^-] = 2.8 \times 10^{-10} mole^2/\ell^2$

This product does not change at constant temperature in an aqueous solution. Therefore,

$[Ag^+][Cl^-] = 2.8 \times 10^{-10} mole^2/\ell^2$

Q-17 With reference to the preceding question, will the final $[Ag^+] = [Cl^-]$? Why?

A-17 No, the final $[Ag^+]$ will not equal the final $[Cl^-]$. In pure water, this would be the case, but with NH_3 present, Ag^+ forms $Ag(NH_3)_2^+$, reducing $[Ag^+]$ so that more AgCl dissolves.

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$
$$Ag^+ \xrightarrow{2NH_3} Ag(NH_3)_2^+$$

Therefore,

$$[Cl^-] >> [Ag^+]$$

Q-18 In reference to the solution described in the preceding answer, what can be said with regard to final concentration of Ag^+, $Ag(NH_3)_2^+$, and Cl^-? Which concentrations are approximately the same?

A-18 $[Cl^-] >> [Ag^+]$, but

$[Cl^-] = [Ag^+] + [Ag(NH_3)_2^+]$.

Because almost all Ag^+ is converted to $Ag(NH_3)_2^+$,

$(K_d = 6 \times 10^{-8} mole^2/\ell^2)$

$[Ag^+]$ must be much, much smaller than $[Ag(NH_3)_2^+]$, therefore, $[Cl^-]$ is approximately equal to $[Ag(NH_3)_2^+]$.

Q-19 If excess solid AgCl is placed in one liter of 0.1 M NH_4OH, what equilibria are involved? What are the equilibrium expressions?

A-19 $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

$$K_{sp} = [Ag^+][Cl^-]$$

$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

Q-20 Combine the equilibrium expressions (K_{sp} and K_d) in such a way as to eliminate a term.

(Hint: The $[Ag^+]$ is equal in the two expressions.)

A-20 $$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = K_d$$

$$[Ag^+] = \frac{K_d[Ag(NH_3)_2^+]}{[NH_3]^2}$$

and

$[Ag^+][Cl^-] = K_{sp}$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]}$$

Since the $[Ag^+]$ is equal in the two expressions

$$\frac{K_{sp}}{[Cl^-]} = \frac{K_d[Ag(NH_3)_2^+]}{[NH_3]^2}$$

and

$$\frac{K_{sp}}{K_d} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

Q-21 What is the reaction described by the expression given in the preceding answer?

A-21 $2NH_3 + AgCl_{(s)} \rightleftarrows Ag(NH_3)_2^+ + Cl^-$

Q-22 By use of the equation in the preceding answer, and the approximation $[Cl^-] = [Ag(NH_3)_2^+]$ (see A-18) calculate how much AgCl will dissolve in one liter of 0 1 M NH_4OH

(Hint Let $\underline{x}$ equal the number of moles of AgCl which dissolve.)

$$K_{diss} = 6 \times 10^{-8}\ mole^2/\ell^2$$
$$K_{sp} = 2\ 8 \times 10^{-10}\ mole^2/\ell^2$$

A-22 $$\frac{K_{sp}}{K_{diss}} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

If $\underline{x}$ = moles of AgCl that dissolved, then

$$\underline{x} = [Cl^-]$$

and approximately

$$\underline{x} = [Ag(NH_3)_2^+]$$

The concentration of $NH_3 = 0\ 1 - 2\underline{x}$ because two moles of NH_3 are required for every mole of $Ag(NH_3)_2^+$ ion formed

$$\frac{K_{sp}}{K_{diss}} = \frac{(\underline{x})(\underline{x})}{(0\ 1 - 2\underline{x})^2} = 5 \times 10^{-3}$$

Taking the square root of each side yields

$$\frac{\underline{x}}{0\ 1 - 2\underline{x}} = 7 \times 10^{-2}$$

$\underline{x} = 6 \times 10^{-3}$ M = moles of AgCl dissolved

A-23 Write a single expression for the equilibrium involved when an excess of solid AgI is added to a 0.1 M NH_4OH solution

K_{sp} for AgI = $8\ 5 \times 10^{-17}\ mole^2/\ell^2$

K_d for $Ag(NH_3)_2^+ = 6 \times 10^{-8}\ mole^2/\ell^2$

A-23 The two equilibria involved in this system are

$$AgI_{(s)} \rightleftarrows Ag^+ + I^-$$
$$K_{sp} = [Ag^+][I^-]$$

and

$$Ag(NH_3)_2 \rightleftarrows Ag^+ + 2NH_3$$
$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

Solving for $[Ag^+]$ in each expression and equating the results yields

$$\frac{K_{sp}}{[I^-]} = \frac{K_d[Ag(NH_3)_2^+]}{[NH_3]^2}$$

$$\frac{K_{sp}}{K_d} = \frac{[Ag(NH_3)_2^+][I^-]}{[NH_3]^2} = 1 \times 10^{-9}$$

The derived equation is for the reaction

$$AgI_{(s)} + 2NH_3 \rightarrow I^- + Ag(NH_3)_2^+$$

Q-24 What approximations can be made for $[NH_3]$, $[I^-]$, and $[Ag(NH_3)_2^+]$ for the situation described in the preceding question?

A-24 The very small equilibrium constant for the reaction involved indicates that very little $AgI_{(s)}$ will be converted to $Ag(NH_3)_2^+$. Therefore, the approximation that $[NH_3]$ remains constant at 0.1 M can be made. Because of the small K_d for $Ag(NH_3)_2^+$ an approximation that all Ag^+ is converted to $Ag(NH_3)_2^+$ is valid.

$$[Ag(NH_3)_2^+] = [I^-]$$

Q-25 Using the approximations given in the preceding answer, calculate the amount of AgI that would dissolve in one liter of 0.1 M NH_4OH.

A-25 $$\frac{[I^-][Ag(NH_3)_2^+]}{[NH_3]^2} = 1 \times 10^{-9}$$

Approximating

$[NH_3] = 0.1$ M and

$[I^-] = [Ag(NH_3)_2^+] = \underline{x}$

$$\frac{x^2}{(0.1)} = 1 \times 10^{-9}$$

$\underline{x} = 3 \times 10^{-6}$ M = moles AgI which dissolve

Q-26 Cadmium forms a complex with NH_3

$$Cd(NH_3)_4^{+2} \rightleftarrows Cd^{+2} + 4NH_3$$

$$K_d = 1 \times 10^{-7}\ \text{mole}^4/\ell^4$$

If excess solid CdS,

$(K_{sp} = 6 \times 10^{-27}\ \text{mole}^2/\ell^2$

$CdS_{(s)} \rightleftarrows Cd^{+2} + S^{-2})$

is added to a 1 M NH_4OH solution, what are the reactions which occur? Combine the equilibrium expressions for these two reactions into a single expression.

A-26 $Cd(NH_3)_4^{+2} \rightleftarrows Cd^{+2} + 4NH_3$

$CdS_{(s)} \rightleftarrows Cd^{+2} + S^{-2}$

$K_{sp} = [Cd^{+2}][S^{-2}]$

$$K_d = \frac{[Cd^{+2}][NH_3]^4}{[Cd(NH_3)_4^{+2}]}$$

Solving for $[Cd^{+2}]$ and equating the result yields

$$\frac{K_{sp}}{K_d} = \frac{[Cd(NH_3)_4^{+2}][S^{-2}]}{[NH_3]^4}$$

$$= 6 \times 10^{-20}\ \ell^2/\text{mole}^2$$

Q-27 What is the reaction described by the expression

$$6 \times 10^{-20}\ \ell^2/\text{mole}^2 = \frac{[S^{-2}][Cd(NH_3)_4^{+2}]}{[NH_3]^4}$$

A-27 $4NH_3 + CdS_{(s)} \rightleftarrows Cd(NH_3)_4^{+2} + S^{-2}$

Q-28 For the solution described in Q-26 give approximate values or relationships for the terms

$[NH_3]$, $[S^{-2}]$, $[Cd(NH_3)_4^{+2}]$ and $[Cd^{+2}]$.

A-28 $[NH_3] = 1$ M

$[S^{-2}] = [Cd(NH_3)_4{}^{+2}] >> [Cd^{+2}]$

Because of the small constant for the reaction given in the preceding answer, very little NH_3 is consumed and approximately

$[NH_3] = 1$ M

Because of the small K_d for $Cd(NH_3)_4{}^{+2}$, very little Cd^{+2} exists in solution, i e , $[Cd^{+2}]$ will be very small as compared to $[Cd(NH_3)_4{}^{+2}]$ For every $Cd(NH_3)_4{}^{+2}$ and Cd^{+2} ion formed, a S^{-2} must form and because

$[Cd^{+2}] << [Cd(NH_3)_4{}^{+2}]$

then approximately,

$[Cd(NH_3)_4{}^{+2}] = [S^{-2}]$

Q-29 Calculate the amount of CdS that will dissolve in one liter of 1 M NH_4OH.

A-29 $\frac{[S^{-2}][Cd(NH_3)_4{}^{+2}]}{[NH_3]^4} = 6 \times 10^{-20}$ (from A-26)

Letting $\underline{x} = [S^{-2}]$ = moles of CdS that dissolve

and making the approximation that

$[S^{-2}] = [Cd(NH_3)_4{}^{+2}]$

$[NH_3] = 1$ M

then,

$\frac{(x)(x)}{(1)^4} = 6 \times 10^{-20}$

$\underline{x} = 2 \times 10^{-10}$ M

Therefore, 2×10^{-10} mole of CdS dissolved in one liter of solution.

Q-30 Zinc hydroxide will dissolve in strongly basic solution because of the reaction

$Zn(OH)_{2(s)} + 2OH^- \rightleftharpoons Zn(OH)_4{}^{-2}$

If the K_{diss} for tetrahydroxo-zincate (II) ion $(Zn(OH)_4{}^{-2})$ is 10 mole/ℓ, what must the final $[OH^-]$ be in order to dissolve 0 1 mole of solid $Zn(OH)_2$ in a liter of basic solution?

K_{sp} for $Zn(OH)_2 = 5 \times 10^{-17}$ mole$^3/\ell^3$

(Hint: $K_{diss(Zn(OH)_4{}^{-2})} \quad \frac{[OH^-]^2}{[Zn(OH)_4{}^{-2}]}$

K_{diss} includes the factor $[Zn(OH)_{2(s)}]$ What is the $[Zn(OH)_4{}^{-2}]$ when all the $Zn(OH)_{2(s)}$ has dissolved?)

A-30 When all the $Zn(OH)_2$ has dissolved,

$[Zn(OH)_4{}^{-2}] = 0.1$ M

Let $\underline{x} = [OH^-]$

$\frac{\underline{x}^2}{0\ 1} = 10$

$\underline{x}^2 = 1$ mole$^2/\ell^2$

$\underline{x} = 1$ M $= [OH^-]$

Q-31 The K_{diss} for trihydroxo-plumbate (II) ion is 50

$Pb(OH)_3{}^- \rightleftharpoons Pb(OH)_{2(s)} + OH^-$

What must the final $[OH^-]$ be in order to dissolve 0 2 mole of solid $Pb(OH)_2$ in a liter of basic solution?

$K_{sp}\ Pb(OH)_2 = 4 \times 10^{-15}$ mole$^3/\ell^3$

(Hint: What is $[Pb(OH)_3{}^-]$ when all $Pb(OH)_2$ has dissolved?)

A-31 When all the $Pb(OH)_2$ has dissolved,

$[Pb(OH)_3{}^-] = 0.2$ M

$K_{diss} = \frac{[OH^-]}{[Pb(OH)_3{}^-]}$

$[OH^-] = 50(0.2) = 10$ M

Q-32 How much $Pb(OH)_2$ would dissolve in 10 ml (0.010 liter) of 1 M NaOH?

(Hint: Let $\underline{x}$ = $Pb(OH)_2$ that dissolved.)

A-32 $[OH^-] = 1 - \underline{x}$

$\underline{x} = [Pb(OH)_3^-]$ = amount of $Pb(OH)_2$ that will dissolve in 1 liter of solution

$$K_{diss} = \frac{1 - \underline{x}}{\underline{x}} = 50$$

$[Pb(OH)_3^-] = 2 \times 10^{-2}$ M = amount of $Pb(OH)_2$ that would dissolve in 1 liter, therefore, 2×10^{-4} mole would dissolve in 10^{-2} liter

Q-33 How much solid $Pb(OH)_2$ would dissolve in 10 ml of 6 M NH_4OH?

$(K_{NH_4OH} = 1.8 \times 10^{-5}$ mole/ℓ)

(Hint What is $[OH^-]$ in NH_4OH solution?)

A-33 $[OH^-]$ in 6 M NH_4OH must be calculated

$$K_{NH_4OH} = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5} \text{ mole}/\ell$$

Let $\underline{x} = [OH^-]$

$(\underline{x})^2 = (6)(1.8 \times 10^{-5}) \text{ mole}^2/\ell^2$

$[OH^-] = 1 \times 10^{-2}$ M

$$K_{Pb(OH)_3^-} = \frac{[OH^-]}{[Pb(OH)_3^-]} = 50$$

$$[Pb(OH)_3^-] = \frac{(1 \times 10^{-2})}{50}$$

$[Pb(OH)_3^-] = 2 \times 10^{-4}$ M

2×10^{-4} moles of $Pb(OH)_2$ would dissolve in a liter of 6 M NH_4OH, and 2×10^{-6} moles would dissolve in 0.01 liter

Q-34 0.05 gram of $Pb(OH)_{2(s)}$ will dissolve in 10 ml of 1 M NaOH

0.0005 gram of $Pb(OH)_{2(s)}$ will dissolve in 10 ml of 6 M NH_4OH

Lead hydroxide is amphoteric because appreciable quantities of it will dissolve in solutions with large OH^- concentration. $Al(OH)_3$ is also amphoteric K_{diss} for $Al(OH)_4^-$ is 2.5×10^{-2}.

$$Al(OH)_4^- \rightarrow OH^- + Al(OH)_3$$

How many moles of solid $Al(OH)_3$ will dissolve in 10 ml of 1 M NaOH? How many grams?

A-34 $[OH^-] = 1 - \underline{x}$

$\underline{x} = [Al(OH)_4^-]$

$$K_{diss} = \frac{[OH^-]}{[Al(OH)_4^-]} = 2.5 \times 10^{-2}$$

$[Al(OH)_4^-] = 1$ M

One mole of $Al(OH)_3$ will dissolve in 1 liter of 1 M NaOH, 0.01 mole will dissolve in 10 ml

$$\frac{0.01 \cancel{\text{ mole } Al(OH)_3}}{} \left| \frac{78 \text{ g}}{1 \cancel{\text{ mole } Al(OH)_3}} \right. = 0.78 \text{ g}$$

Q-35 $Sn(OH)_{2(s)}$ is amphoteric If the K_{diss} of $Sn(OH)_3^-$ is 2×10^3, what must $[OH^-]$ be in order to dissolve 2×10^{-5} mole of $Sn(OH)_{2(s)}$ in 10 ml of basic solution?

$$Sn(OH)_3^- \rightarrow Sn(OH)_2 + OH^-$$

A-35 $[Sn(OH)_3^-] = 2 \times 10^{-3}$ M

$$K_{diss} = \frac{[OH^-]}{(2 \times 10^{-3})} = 2 \times 10^3$$

$[OH^-] = 4.0$ M

IONIZATION CONSTANTS OF WEAK ACIDS

Acid	Equilibrium	Ionization Constant (at 25°C)
Acetic	$CH_3COOH = H^+ + CH_3COO^-$	1.85×10^{-5}
Arsenic	$H_3AsO_4 = H^+ + H_2AsO_4^-$	2.5×10^{-4}
Dihydrogen arsenate ion	$H_2AsO_4^- = H^+ + HAsO_4^{--}$	5.6×10^{-8}
Monohydrogen arsenate ion	$HAsO_4^{--} = H^+ + AsO_4^{---}$	3.0×10^{-13}
Arsenous	$H_3AsO_3 = H^+ + H_2AsO_3^-$	6.0×10^{-10}
Benzoic	$C_6H_5COOH = H^+ + C_6H_5COO^-$	6.6×10^{-5}
Boric	$H_3BO_3 = H^+ + H_2BO_3^-$	6.0×10^{-10}
Carbonic	$H_2CO_3 = H^+ + HCO_3^-$	4.2×10^{-7}
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{--}$	4.8×10^{-11}
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{--}$	1.26×10^{-2}
Chloracetic	$ClCH_2COOH = H^+ + ClCH_2COO^-$	1.4×10^{-3}
Chlorous	$HClO_2 = H^+ + ClO_2^-$	1.1×10^{-2}
Bicuprate ion	$HCuO_2^- = H^+ + CuO_2^{--}$	8×10^{-14}
Cyanic	$HCNO = H^+ + CNO^-$	2.0×10^{-4}
Dichloracetic	$Cl_2CHCOOH = H^+ + Cl_2CHCOO^-$	5.5×10^{-2}
Formic	$HCOOH = H^+ + HCOO^-$	2.1×10^{-4}
Hydrazoic	$HN_3 = H^+ + N_3^-$	1.9×10^{-5}
Hydrocyanic	$HCN = H^+ + CN^-$	4.0×10^{-10}
Hydrofluoric	$HF = H^+ + F^-$	6.9×10^{-4}
Hydrogen peroxide	$H_2O_2 = H^+ + HO_2^-$	2.4×10^{-12}
Hydrogen selenide	$H_2Se = H^+ + HSe^-$	1.9×10^{-4}
Hydrogen sulfide	$H_2S = H^+ + HS^-$	1.0×10^{-7}
Bisulfide ion	$HS^- = H^+ + S^{--}$	1.3×10^{-13}
Hydrogen telluride	$H_2Te = H^+ + HTe^-$	2.5×10^{-3}
Bitelluride ion	$HTe^- = H^+ + Te^{--}$	1.0×10^{-11}
Hypobromous	$HBrO = H^+ + BrO^-$	2×10^{-9}
Hypochlorous	$HClO = H^+ + ClO^-$	3.2×10^{-8}
Nitrous	$HNO_2 = H^+ + NO_2^-$	4.5×10^{-4}
o-Nitrobenzoic	$C_7H_5NO_4 = H^+ + C_7H_4NO_4^-$	6.1×10^{-3}
Oxalic	$H_2C_2O_4 = H^+ + HC_2O_4^-$	3.8×10^{-2}
Monohydrogen oxalate ion	$HC_2O_4^- = H^+ + C_2O_4^{--}$	5.0×10^{-5}
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	1.0×10^{-10}
Phosphoric	$H_3PO_4 = H^+ + H_2PO_4^-$	7.5×10^{-3}
Dihydrogen phosphate ion	$H_2PO_4^- = H^+ + HPO_4^{--}$	6.2×10^{-8}
Monohydrogen phosphate ion	$HPO_4^{--} = H^+ + PO_4^{---}$	1×10^{-12}
Phosphorous	$H_3PO_3 = H^+ + H_2PO_3^-$	1.6×10^{-2}
Dihydrogen phosphite ion	$H_2PO_3^- = H^+ + HPO_3^{--}$	7.0×10^{-7}
Propionic	$C_2H_5COOH = H^+ + C_2H_5COO^-$	1.4×10^{-5}
Salicylic	$C_7H_6O_3 = H^+ + C_7H_5O_3^-$	1.1×10^{-3}
Selenious	$H_2SeO_3 = H^+ + HSeO_3^-$	2.7×10^{-3}
Biselenate ion	$HSeO_3^- = H^+ + SeO_3^{--}$	2.5×10^{-7}
Sulfurous	$H_2SO_3 = H^+ + HSO_3^-$	1.25×10^{-2}
Bisulfite ion	$HSO_3^- = H^+ + SO_3^{--}$	5.6×10^{-8}
Tartaric	$C_4H_4O_6H_2 = H^+ + C_4H_4O_6H^-$	1.1×10^{-3}
Bitartrate ion	$C_4H_4O_6H^- = H^+ + C_4H_4O_6^{--}$	6.9×10^{-5}
Telluric	$H_2TeO_4 = H^+ + HTeO_4^-$	6×10^{-7}
Bitellurate ion	$HTeO_4^- = H^+ + TeO_4^{--}$	4×10^{-11}
Tellurous	$H_2TeO_3 = H^+ + HTeO_3^-$	2×10^{-3}
Bitellurite ion	$HTeO_3^- = H^+ + TeO_3^{--}$	1×10^{-8}
Aluminum hydroxide	$Al(OH)_3 = H^+ + AlO_2^- + H_2O$	4×10^{-13}
Antimony hydroxide	$Sb(OH)_3 = H^+ + SbO_2^- + H_2O$	1×10^{-11}
Chromium hydroxide	$Cr(OH)_3 = H^+ + CrO_2^- + H_2O$	1×10^{-16}
Cobaltous hydroxide	$Co(OH)_2 = H^+ + HCoO_2^-$	8×10^{-20}
Bicuprate ion	$HCuO_2^- = H^+ + CuO_2^{--}$	8×10^{-14}
Cupric hydroxide	$H_2CuO_2 = H^+ + HCuO_2^-$	1.5×10^{-16}

Acid	Equilibrium	Ionization Constant (at 25°C)
Lead hydroxide	$Pb(OH)_2 = H^+ + HPbO_2^-$	2×10^{-16}
Manganous hydroxide	$Mn(OH)_2 = H^+ + HMnO_2^-$	1×10^{-19}
Mercuric hydroxide	$Hg(OH)_2 = H^+ + HHgO_2^-$	1×10^{-15}
Nickelous hydroxide	$Ni(OH)_2 = H^+ + HNiO_2^-$	6×10^{-19}
Silver hydroxide	$AgOH = H^+ + AgO^-$	2×10^{-18}
Stannous hydroxide	$Sn(OH)_2 = H^+ + HSnO_2^-$	4×10^{-15}
Zinc hydroxide	$Zn(OH)_2 = 2H^+ + ZnO_2^{--}$	1×10^{-29}
	$Zn(OH)_{2(s)} = Zn(OH)^+ + OH^-$	1.2×10^{-12}
	$Zn(OH)^+ = Zn^{++} + OH^-$	4×10^{-5}

IONIZATION CONSTANTS OF WEAK BASES

Base	Equilibrium	Ionization Constant (at 25°C)
Ammonium hydroxide	$NH_4OH = NH_4^+ + OH^-$	1.8×10^{-5}
Methyl ammonium hydroxide	$CH_3NH_3OH = CH_3NH_3^+ + OH^-$	5×10^{-4}
Dimethyl ammonium hydroxide	$(CH_3)_2NH_2OH = (CH_3)_2NH_2^+ + OH^-$	$7\ 4 \times 10^{-4}$
Trimethyl ammonium hydroxide	$(CH_3)_3NHOH = (CH_3)_3NH^+ + OH^-$	7.4×10^{-5}
Ethyl ammonium hydroxide	$C_2H_5NH_3OH = C_2H_5NH_3^+ + OH^-$	5.6×10^{-4}
Phenyl ammonium hydroxide	$C_6H_5NH_3OH = C_6H_5NH_3^+ + OH^-$	4.6×10^{-10}
Hydrazine hydroxide	$H_2NNH_3OH = H_2NNH_3^+ + OH^-$	9.8×10^{-7}
Zinc hydroxide	(1) $Zn(OH)_{2(s)} = Zn(OH)^+ + OH^-$	$1\ 2 \times 10^{-12}$
	(2) $Zn(OH)^+ = Zn^+ + OH^-$	4×10^{-5}

SOLUBILITY PRODUCT CONSTANTS AT 25°C

Substance	Equilibrium	Solubility Product Constant
Acetates		
Silver acetate	$CH_3COOAg_{(s)} = Ag^+ + CH_3COO^-$	4×10^{-3}
Bromates		
Silver bromate	$AgBrO_{3(s)} = Ag^+ + BrO_3^-$	6×10^{-5}
Bromides		
Cuprous bromide	$CuBr_{(s)} = Cu^+ + Br^-$	6×10^{-9}
Lead bromide	$PbBr_{2(s)} = Pb^{++} + 2Br^-$	4.6×10^{-6}
Mercurous bromide	$Hg_2Br_{2(s)} = Hg_2^{++} + 2Br^-$	1.3×10^{-22}
Silver bromide	$AgBr_{(s)} = Ag^+ + Br^-$	5×10^{-13}
Carbonates		
Barium carbonate	$BaCO_{3(s)} = Ba^{++} + CO_3^{--}$	1.6×10^{-9}
Cadmium carbonate	$CdCO_{3(s)} = Cd^{++} + CO_3^{--}$	5.2×10^{-12}
Calcium carbonate	$CaCO_{3(s)} = Ca^{++} + CO_3^{--}$	6.9×10^{-9}
Cobalt carbonate	$CoCO_{3(s)} = Co^{++} + CO_3^{--}$	8×10^{-13}
Cupric carbonate	$CuCO_{3(s)} = Cu^{++} + CO_3^{--}$	2.5×10^{-10}
Lead carbonate	$PbCO_{3(s)} = Pb^{++} + CO_3^{--}$	1.5×10^{-13}
Magnesium carbonate	$MgCO_{3(s)} = Mg^{++} + CO_3^{--}$	4×10^{-5}

Substance	Equilibrium	Solubility Product Constant
Manganous carbonate	$MnCO_{3(s)} = Mn^{++} + CO_3^{--}$	9×10^{-11}
Mercurous carbonate	$Hg_2CO_{3(s)} = Hg_2^{++} + CO_3^{--}$	9×10^{-17}
Nickelous carbonate	$NiCO_{3(s)} = Ni^{++} + CO_3^{--}$	1.4×10^{-7}
Silver carbonate	$Ag_2CO_{3(s)} = 2Ag^{+} + CO_3^{--}$	8.2×10^{-12}
Strontium carbonate	$SrCO_{3(s)} = Sr^{++} + CO_3^{--}$	7×10^{-10}
Zinc carbonate	$ZnCO_{3(s)} = Zn^{++} + CO_3^{--}$	2×10^{-10}
Chlorides		
Cuprous chloride	$CuCl_{(s)} = Cu^{+} + Cl^{-}$	3.2×10^{-7}
Lead chloride	$PbCl_{2(s)} = Pb^{++} + 2Cl^{-}$	1.6×10^{-5}
Mercurous chloride	$Hg_2Cl_{2(s)} = Hg_2^{++} + 2Cl^{-}$	1.1×10^{-18}
Silver chloride	$AgCl_{(s)} = Ag^{+} + Cl^{-}$	2.8×10^{-10}
Chromates		
Barium chromate	$BaCrO_{4(s)} = Ba^{++} + CrO_4^{--}$	8.5×10^{-11}
Calcium chromate	$CaCrO_{4(s)} = Ca^{++} + CrO_4^{--}$	7.1×10^{-4}
Lead chromate	$PbCrO_{4(s)} = Pb^{++} + CrO_4^{--}$	2.0×10^{-16}
Mercurous chromate	$Hg_2CrO_{4(s)} = Hg_2^{++} + CrO_4^{--}$	2×10^{-9}
Silver chromate	$Ag_2CrO_{4(s)} = 2Ag^{+} + CrO_4^{--}$	1.9×10^{-12}
Strontium chromate	$SrCrO_{4(s)} = Sr^{++} + CrO_4^{--}$	3.6×10^{-5}
Cyanides		
Mercurous cyanide	$Hg_2(CN)_{2(s)} = Hg_2^{++} + 2CN^{-}$	5×10^{-40}
Silver cyanide	$AgCN_{(s)} = Ag^{+} + CN^{-}$	1.6×10^{-14}
Fluorides		
Barium fluoride	$BaF_{2(s)} = Ba^{++} + 2F^{-}$	2.4×10^{-5}
Calcium fluoride	$CaF_{2(s)} = Ca^{++} + 2F^{-}$	1.7×10^{-10}
Lead fluoride	$PbF_{2(s)} = Pb^{++} + 2F^{-}$	4×10^{-8}
Magnesium fluoride	$MgF_{2(s)} = Mg^{++} + 2F^{-}$	8×10^{-8}
Strontium fluoride	$SrF_{2(s)} = Sr^{++} + 2F^{-}$	7.9×10^{-10}
Hydroxides		
Aluminum hydroxide	$Al(OH)_{3(s)} = Al^{+++} + 3OH^{-}$	5×10^{-33}
Cadmium hydroxide	$Cd(OH)_{2(s)} = Cd^{++} + 2OH^{-}$	2.0×10^{-14}
Chromic hydroxide	$Cr(OH)_{3(s)} = Cr^{+++} + 3OH^{-}$	7×10^{-31}
Chromous hydroxide	$Cr(OH)_{2(s)} = Cr^{++} + 2OH^{-}$	1×10^{-17}
Cobaltic hydroxide	$Co(OH)_{3(s)} = Co^{+++} + 3OH^{-}$	1×10^{-43}
Cobaltous hydroxide	$Co(OH)_{2(s)} = Co^{++} + 2OH^{-}$	2.5×10^{-16}
Cupric hydroxide	$Cu(OH)_{2(s)} = Cu^{++} + 2OH^{-}$	1.6×10^{-19}
Ferric hydroxide	$Fe(OH)_{3(s)} = Fe^{+++} + 3OH^{-}$	6×10^{-38}
Ferrous hydroxide	$Fe(OH)_{2(s)} = Fe^{++} + 2OH^{-}$	2×10^{-15}
Lead hydroxide	$Pb(OH)_{2(s)} = Pb^{++} + 2OH^{-}$	4×10^{-15}
Magnesium hydroxide	$Mg(OH)_{2(s)} = Mg^{++} + 2OH^{-}$	8.9×10^{-12}
Manganese hydroxide	$Mn(OH)_{2(s)} = Mn^{++} + 2OH^{-}$	2×10^{-13}
Manganic hydroxide	$Mn(OH)_{3(s)} = Mn^{+++} + 3OH^{-}$	1×10^{-36}
Mercuric hydroxide	$HgO_{(s)} + H_2O = Hg^{++} + 2OH^{-}$	3×10^{-26}
Nickel hydroxide	$Ni(OH)_{2(s)} = Ni^{++} + 2OH^{-}$	1.6×10^{-16}
Silver hydroxide	$\frac{1}{2}Ag_2O_{(s)} + \frac{1}{2}H_2O = Ag^{+} + OH^{-}$	1×10^{-8}
Stannous hydroxide	$Sn(OH)_{2(s)} = Sn^{++} + 2OH^{-}$	3×10^{-27}
Zinc hydroxide	$Zn(OH)_{2(s)} = Zn^{++} + 2OH^{-}$	5×10^{-17}
Iodates		
Barium iodate	$Ba(IO_3)_{2(s)} = Ba^{++} + 2IO_3^{-}$	1.3×10^{-9}
Calcium iodate	$Ca(IO_3)_{2(s)} = Ca^{++} + 2IO_3^{-}$	1.7×10^{-6}
Cupric iodate	$Cu(IO_3)_{2(s)} = Cu^{++} + 2IO_3^{-}$	1.4×10^{-7}

Substance	Equilibrium	Solubility Product Constant
Lead iodate	$Pb(IO_3)_{2(s)} = Pb^{++} + 2IO_3^-$	2.6×10^{-13}
Mercuric iodate	$Hg(IO_3)_{2(s)} = Hg^{++} + 2IO_3^-$	3×10^{-13}
Mercurous iodate	$Hg_2(IO_3)_{2(s)} = Hg_2^{++} + 2IO_3^-$	1.9×10^{-14}
Silver iodate	$AgIO_{3(s)} = Ag^+ + IO_3^-$	3×10^{-8}
Iodides		
Cuprous iodide	$CuI_{(s)} = Cu^+ + I^-$	1×10^{-12}
Lead iodide	$PbI_{2(s)} = Pb^{++} + 2I^-$	8.3×10^{-9}
Mercurous iodide	$Hg_2I_{2(s)} = Hg_2^{++} + 2I^-$	4×10^{-29}
Silver iodide	$AgI_{(s)} = Ag^+ + I^-$	8.5×10^{-17}
Thallous iodide	$TlI_{(s)} = Tl^+ + I^-$	2.5×10^{-8}
Oxalates		
Barium oxalate	$BaC_2O_{4(s)} = Ba^{++} + C_2O_4^{--}$	1.5×10^{-8}
Cadmium oxalate	$CdC_2O_{4(s)} = Cd^{++} + C_2O_4^{--}$	1.5×10^{-8}
Calcium oxalate	$CaC_2O_{4(s)} = Ca^{++} + C_2O_4^{--}$	1.3×10^{-9}
Cupric oxalate	$CuC_2O_{4(s)} = Cu^{++} + C_2O_4^{--}$	3×10^{-8}
Ferrous oxalate	$FeC_2O_{4(s)} = Fe^{++} + C_2O_4^{--}$	2×10^{-7}
Lead oxalate	$PbC_2O_{4(s)} = Pb^{++} + C_2O_4^{--}$	8.3×10^{-12}
Magnesium oxalate	$MgC_2O_{4(s)} = Mg^{++} + C_2O_4^{--}$	8.6×10^{-5}
Manganic oxalate	$Mn_2(C_2O_4)_{3(s)} = 2Mn^{+++} + 3C_2O_4^{--}$	7×10^{-20}
Manganous oxalate	$MnC_2O_{4(s)} = Mn^{++} + C_2O_4^{--}$	1×10^{-15}
Mercurous oxalate	$Hg_2C_2O_{4(s)} = Hg_2^{++} + C_2O_4^{--}$	1×10^{-13}
Silver oxalate	$Ag_2C_2O_{4(s)} = 2Ag^+ + C_2O_4^{--}$	1×10^{-11}
Strontium oxalate	$SrC_2O_{4(s)} = Sr^{++} + C_2O_4^{--}$	5.6×10^{-8}
Zinc oxalate	$ZnC_2O_{4(s)} = Zn^{++} + C_2O_4^{--}$	1.5×10^{-9}
Sulfates		
Barium sulfate	$BaSO_{4(s)} = Ba^{++} + SO_4^{--}$	1.5×10^{-9}
Calcium sulfate	$CaSO_{4(s)} = Ca^{++} + SO_4^{--}$	2.4×10^{-5}
Lead sulfate	$PbSO_{4(s)} = Pb^{++} + SO_4^{--}$	1.3×10^{-8}
Strontium sulfate	$SrSO_{4(s)} = Sr^{++} + SO_4^{--}$	7.6×10^{-7}
Sulfides		
Bismuth sulfide	$Bi_2S_{3(s)} = 2Bi^{+++} + 3S^{--}$	1×10^{-70}
Cadmium sulfide	$CdS_{(s)} = Cd^{++} + S^{--}$	6×10^{-27}
Cobalt sulfide	$CoS_{(s)} = Co^{++} + S^{--}$	5×10^{-22}
Cupric sulfide	$CuS_{(s)} = Cu^{++} + S^{--}$	4×10^{-36}
Ferrous sulfide	$FeS_{(s)} = Fe^{++} + S^{--}$	4×10^{-17}
Lead sulfide	$PbS_{(s)} = Pb^{++} + S^{--}$	4×10^{-26}
Manganous sulfide	$MnS_{(s)} = Mn^{++} + S^{--}$	8×10^{-14}
Mercuric sulfide	$HgS_{(s)} = Hg^{++} + S^{--}$	1×10^{-50}
Mercurous sulfide	$Hg_2S_{(s)} = Hg_2^{++} + S^{--}$	1×10^{-45}
Nickelous sulfide	$NiS_{(s)} = Ni^{++} + S^{--}$	1×10^{-22}
Silver sulfide	$Ag_2S_{(s)} = 2Ag^+ + S^{--}$	1×10^{-50}
Thallous sulfide	$Tl_2S_{(s)} = 2Tl^+ + S^{--}$	1×10^{-22}
Zinc sulfide	$ZnS_{(s)} = Zn^{++} + S^{--}$	1×10^{-20}
Thiocyanates		
Cuprous thiocyanate	$CuCNS_{(s)} = Cu^+ + CNS^-$	4×10^{-14}
Mercurous thiocyanate	$Hg_2(CNS)_{2(s)} = Hg_2^{++} + 2CNS^-$	3×10^{-20}
Silver thiocyanate	$AgCNS_{(s)} = Ag^+ + CNS^-$	1×10^{-12}

DISSOCIATION CONSTANTS OF COMPLEX IONS

Equilibrium		Dissociation Constant
AlF_6^{---}	$= Al^{+++} + 6F^-$	$1\ 5 \times 10^{-20}$
AlF_5^{--}	$= Al^{+++} + 5F^-$	4.3×10^{-20}
AlF_4^-	$= Al^{+++} + 4F^-$	2×10^{-18}
$Cd(NH_3)_4^{++}$	$= Cd^{++} + 4NH_3$	1×10^{-7}
$Cd(CN)_4^{--}$	$= Cd^{++} + 4CN^-$	1×10^{-19}
CdI_4^{--}	$= Cd^{++} + 4I^-$	5×10^{-7}
$CdCl_3^-$	$= Cd^{++} + 3Cl^-$	4×10^{-3}
$Co(NH_3)_6^{++}$	$= Co^{++} + 6NH_3$	1.25×10^{-5}
$Co(NH_3)_6^{+++}$	$= Co^{+++} + 6NH_3$	2.2×10^{-34}
$Co(NH_3)_5H_2O^{+++}$	$= Co^{+++} + 5NH_3 + H_2O$	1.6×10^{-35}
$Co(NH_3)_5Cl^{++}$	$= Co^{+++} + 5NH_3 + Cl^-$	1×10^{-38}
$Cu(CN)_2^-$	$= Cu^+ + 2CN^-$	1×10^{-16}
$Cu(NH_3)^+$	$= Cu^+ + NH_3$	7×10^{-7}
$Cu(NH_3)_2^+$	$= Cu^+ + 2NH_3$	1.4×10^{-11}
$Cu(CN)_4^{---}$	$= Cu^+ + 4CN^-$	2×10^{-27}
$Cu(NH_3)_4^{++}$	$= Cu^{++} + 4NH_3$	5×10^{-15}
$Cu(C_2O_4)_2^{--}$	$= Cu^{++} + 2C_2O_4^{--}$	5×10^{-11}
$Fe(CN)_6^{----}$	$= Fe^{++} + 6CN^-$	1×10^{-35}
$Fe(CN)_6^{---}$	$= Fe^{+++} + 6CN^-$	1×10^{-42}
FeF_5^{--}	$= Fe^{+++} + 5F^-$	5×10^{-16}
$FeCNS^{++}$	$= Fe^{+++} + CNS^-$	1×10^{-3}
$Fe(CNS)_6^{---}$	$= Fe^{+++} + 6CNS^-$	8×10^{-10}
$PbCl_3^-$	$= Pb^{++} + 3Cl^-$	4.2×10^{-2}
PbI_3^-	$= Pb^{++} + 3I^-$	3.6×10^{-6}
$Mn(C_2O_4)^+$	$= Mn^{+++} + C_2O_4^{--}$	1×10^{-10}
$Mn(C_2O_4)_2^-$	$= Mn^{+++} + 2C_2O_4^{--}$	2.5×10^{-17}
$Mn(C_2O_4)_3^{---}$	$= Mn^{+++} = 3C_2O_4^{--}$	7×10^{-20}
$Hg(CN)_4^{--}$	$= Hg^{++} + 4CN^-$	4×10^{-42}
HgI_4^{--}	$= Hg^{++} + 4I^-$	5×10^{-31}
$HgBr_4^{--}$	$= Hg^{++} + 4Br^-$	2.3×10^{-22}
$HgCl_4^{--}$	$= Hg^{++} + 4Cl^-$	1×10^{-16}
$Hg(CNS)_4^{--}$	$= Hg^{++} + 4CNS^-$	5×10^{-20}
$Ni(NH_3)_4^{++}$	$= Ni^{++} + 4NH_3$	1×10^{-8}
$Ni(NH_3)_6^{++}$	$= Ni^{++} + 6NH_3$	1.8×10^{-9}
$Ni(CN)_4^{--}$	$= Ni^{++} + 4CN^-$	1×10^{-22}
$Ag(SO_3)_2^{---}$	$= Ag^+ + 2SO_3^{--}$	2×10^{-9}
$Ag(NH_3)_2^+$	$= Ag^+ + 2NH_3$	6×10^{-8}
$Ag(S_2O_3)_2^{---}$	$= Ag^+ + 2S_2O_3^{--}$	6×10^{-14}
$Ag(CN)_2^-$	$= Ag^+ + 2CN^-$	1.8×10^{-19}
SnF_6^{--}	$= Sn^{++++} + 6F^-$	1×10^{-18}
$Zn(NH_3)_4^{++}$	$= Zn^{++} + 4NH_3$	3.4×10^{-10}
$Zn(CN)_4^{--}$	$= Zn^{++} + 4CN^-$	1×10^{-18}

Chapter 9 | *ELECTROCHEMISTRY*

Part I Galvanic Cells and the Nernst Equation

After completing this section, you should be able to

a) write the half-reactions occurring at the anode and the cathode of a galvanic cell
b) calculate the emf for a cell from the standard electrode potentials of the half-cells
c) calculate free energy changes and equilibrium constants from the emf of a cell
d) calculate the emf of galvanic cells containing solutions of various concentrations

Part II: Electrolytic Cells and Faraday's Law

After completing this section, you should be able to

a) write the reactions occurring at the anode and cathode of an electrolytic cell
b) calculate the amount of material oxidized and reduced by a given quantity of electricity.

Part III: Oxidation Potentials

After completing this section you should

a) understand the relationship between ionization energy, hydration energy, sublimation energy, and oxidation potential
b) understand why oxidation potentials, unlike ionization energies, show no well defined periodic trends.

Part IV: Balancing Oxidation-Reduction Equations

After completing this section you should be able to balance oxidation-reduction equations by the "half-reaction" method.

PART I: Galvanic Cells and the Nernst Equation

S-1 When a piece of sodium metal is dropped into water, a reaction takes place to yield sodium hydroxide and hydrogen

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

In this reaction, electrons are transferred from sodium atoms to water molecules. A reaction which involves the transfer of electrons is called an oxidation-reduction (redox) reaction. The substance which loses electrons is said to be oxidized and the substance which gains electrons is said to be reduced.

	Q-1 In the redox reaction between Na and H_2O, what substance is oxidized?
A-1 Na. Sodium loses electrons	Q-2 In the previous reaction, Na loses an electron to form Na^+. Write in equation form a reaction showing the oxidation of Na. (Hint: Write the electron as e^-.)
A-2 $Na \rightarrow Na^+ + e^-$	Q-3 In the redox reaction between Na and H_2O, what substance is reduced?
A-3 H_2O. Water gains an electron to form hydrogen and OH^-	Q-4 The oxidation and reduction reactions in an electron transfer reaction are called half-cell reactions. Write the half-cell reaction for the reduction of H_2O in the reaction between Na and H_2O. (Is e^- a reactant or product?)
A-4 $H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$	Q-5 When a piece of copper metal is placed in a solution of silver nitrate (Ag^+ and NO_3^- ions), silver metal deposits on the surface of the copper. The redox reaction is given by the equation $2Ag^+ + Cu \rightarrow Cu^{+2} + 2Ag$. Is copper metal oxidized or reduced?
A-5 Copper loses electrons in forming Cu^{+2}; therefore, copper is oxidized.	Q-6 Write a half-cell reaction for the oxidation of copper.
A-6 $Cu \rightarrow Cu^{+2} + 2e^-$	Q-7 In the reaction between Ag^+ and Cu, are the silver ions oxidized or reduced?
A-7 Silver ions gain electrons in forming Ag, therefore, silver ions are reduced.	Q-8 Write a half-cell reaction for the reduction of Ag^+ ions.

A-8 $Ag^+ + e^- \rightarrow Ag$

Q-9 When a piece of zinc metal is placed in a solution of copper sulfate (Cu^{+2} and SO_4^{-2} ions), copper metal plates out on the zinc The redox reaction is given by the equation

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$$

Write the two half-cell reactions labeling the oxidation and reduction reactions

A-9 $Zn \rightarrow Zn^{+2} + 2e^-$ oxidation

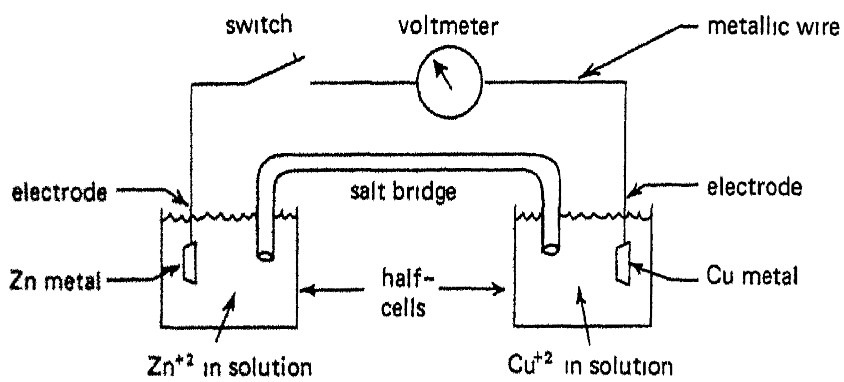
$Cu^{+2} + 2e^- \rightarrow Cu$ reduction

R a) **Electron transfer reactions result in oxidation and reduction.**

b) **Oxidation is the loss of electrons.**

c) **Reduction is the gain of electrons.**

S-2 Chemical energy can be converted into electrical energy when a redox reaction is carried out with the reactants separated in space and connected only by an electrical conductor This type of arrangement is called a galvanic cell Consider the copper-zinc reaction from Q-9. The galvanic cell for this system is diagrammed below



a) The electrode provides electrical contact between the solutions and the external circuit.

b) The salt bridge is a tube filled with a concentrated solution of KCl or NH_4NO_3 which permits electrical contact between the solutions by means of ionic conductance (movement of ions) but prevents the solutions from mixing

c) The voltmeter is a device for measuring the potential for a reaction to take place, i.e., potential difference between the two electrodes

Q-10 When the switch is closed, current flows through the wire. If copper metal is deposited on the copper electrode, what must be happening to the Cu^{+2} ions in solution?

A-10 Cu^{+2} ions are diffusing to the Cu electrode where they are reduced and become Cu metal.

Q-11 Write an equation for the reaction occurring at the copper electrode

A-11 $Cu^{+2} + 2e^- \rightarrow Cu$

This compartment of the cell is called the <u>reduction</u> half-cell

Q-12 If the zinc electrode loses mass, what reaction must be occurring at the zinc electrode?

A-12 $Zn \rightarrow Zn^{+2} + 2e^-$

This compartment of the cell is called the <u>oxidation</u> half-cell

Q-13 Current is defined as the flow of electrons. In which direction are electrons flowing through the external circuit of the cell described in S 2?

A-13 Electrons flow from the Zn electrode through the wire to the Cu electrode where Cu^{+2} ions gain electrons and are reduced

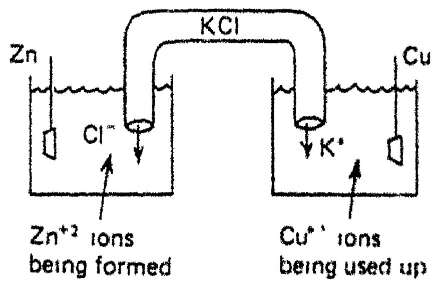
Q-14 Electrons are negatively charged and flow from regions of negative charge to regions of positive charge. On this basis, which electrode has a positive charge and which electrode has a negative charge?

A-14 Electrons flow from the Zn electrode to the Cu electrode. Therefore, Zn is negative and Cu is positive.

Q-15 As the reaction proceeds, the concentration of Cu^{++} ions is decreased in one half cell while the concentration of Zn^{++} ions is increased in the other half-cell. Electrical neutrality is maintained in the two solutions. How?

(Hint: Remember the salt bridge with a high concentration of KCl in it.)

A-15 Electrical neutrality is maintained in the two solutions by means of the salt bridge. K^+ ions will migrate into one cell and Cl^- ions into the other

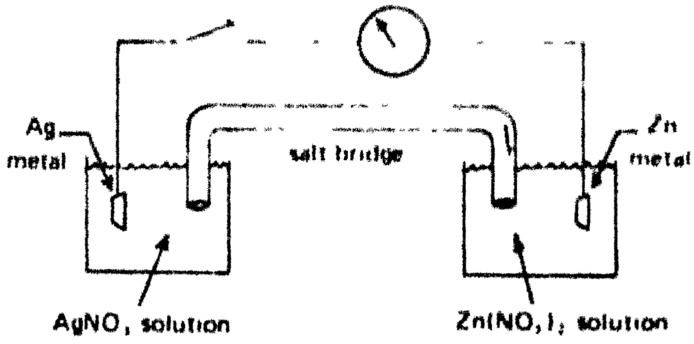


Q-16 The two electrodes in a galvanic cell are called the <u>anode</u> and the <u>cathode</u>. Reduction occurs at the cathode and oxidation at the anode. In the Cu Zn cell, which electrode is the anode and which is the cathode?

A-16 Cu electrode is the cathode.

Zn electrode is the anode.

Q-17 Consider the following cell



If Ag metal is deposited on the Ag electrode and the zinc electrode loses mass, label the anode and cathode.

A-17 Ag - cathode
Zn - anode

Q-18 Write the reactions occurring at each electrode

A-18 $Ag^{+} + e^{-} \rightarrow Ag$
$Zn \rightarrow Zn^{+2} + 2e^{-}$

Q-19 In which direction do electrons flow through the external circuit?

A-19 Electrons flow from the zinc electrode to the silver electrode

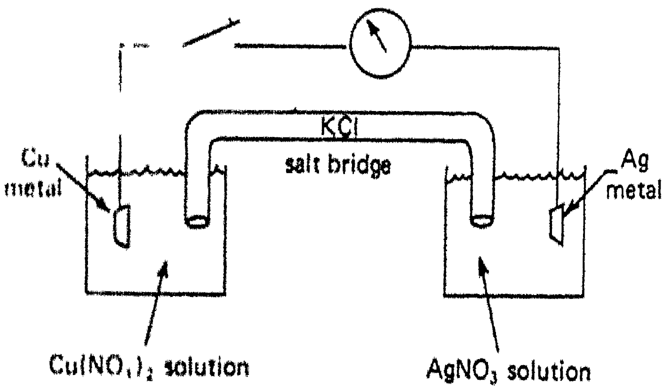
Q-20 How is neutrality maintained in the solutions of the two half-cells?

A-20 Cl^{-} ions flow out of the salt bridge into the Zn electrode compartment, and K^{+} ions flow out of the salt bridge into the Ag electrode compartment

Q-21 Diagram a galvanic cell which would have the overall chemical reaction

$$2Ag^{+} + Cu \rightarrow Cu^{+2} + 2Ag$$

A-21



Q-22 Write the reaction occurring at the anode.

A-22 $Cu \rightarrow Cu^{+2} + 2e^{-}$

Q-23 Write the reaction occurring at the cathode.

A-23 $Ag^{+} + e^{-} \rightarrow Ag$

Q-24 In which direction do electrons flow through the external circuit?

A-24 From the Cu electrode to the Ag electrode.

R
a) Chemical energy can be converted to electrical energy by use of a galvanic cell.
b) Reduction occurs at the cathode.
c) Oxidation occurs at the anode.
d) In a galvanic cell the cathode is the positive electrode while the anode is the negative electrode.
e) Electrons flow through the external circuit from the negative electrode to the positive electrode.

S-3 The cell diagrammed in S-2 can be represented schematically as

$$Zn \mid Zn^{+2} \parallel Cu^{+2} \mid Cu$$

where a single line represents a phase boundary (i e solid Zn electrode and Zn^{+2} ions in solution) and a double line a salt bridge By convention, the oxidation half-cell is written first

Q-25 Represent the cell from Q-17 schematically.

A-25 $Zn \mid Zn^{+2} \parallel Ag^{+} \mid Ag$

Q-26 Represent the cell from A-21 schematically.

A-26 $Cu \mid Cu^{+2} \parallel Ag^{+} \mid Ag$

Q-27 Represent schematically a cell which has the overall reaction

$$Sn + Cu^{+2} \rightarrow Sn^{+2} + Cu.$$

A-27 $Sn \mid Sn^{+2} \parallel Cu^{+2} \mid Cu$

Q-28 Represent schematically a cell which has the overall reaction

$$Fe + Sn^{+2} \rightarrow Fe^{+2} + Sn$$

A-28 $Fe \mid Fe^{+2} \parallel Sn^{+2} \mid Sn$

R A galvanic cell can be represented schematically as

$$Zn \mid Zn^{+2} \parallel Cu^{+2} \mid Cu$$

with the oxidation half-cell on the left and the reduction half-cell on the right.

S-4 A difference in potential causes current to flow from an electrode of higher potential to one of lower potential. This difference is called the electromotive force (emf). It is measured directly with a voltmeter and is given the units of volts. Since the absolute value for the emf of a single half-cell reaction can't be determined, it is related to a reference electrode The reference is the hydrogen electrode which has a defined emf of 0.00(E_{H_2} 0.00 volts) The emf of any other electrode reaction can be determined by measuring the emf of a cell constructed from the electrode in question and a hydrogen electrode. The following convention is used.

a) The cell is written such that the oxidation half-cell is on the left and reduction on the right

b) The emf is called positive if electrons flow from left to right through the external circuit.

Q-29 The hydrogen electrode has been chosen as the reference electrode in electrochemical measurements. Write a half-cell reaction for the reduction of H^+ ions.

A-29 $2H^+ + 2e^- \rightarrow H_2$

Q-30 What is the potential for H^+ ions to be reduced?

A-30 By convention, this has been given a value of zero

$E_{H_2} = 0.00$ volts

Q-31 Write a half-cell reaction for the oxidation of H_2 gas molecules

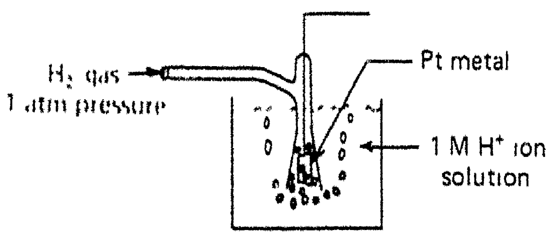
A-31 $H_2 \rightarrow 2H^+ + 2e^-$

Q-32 What is the potential for H_2 molecules to be oxidized?

A-32 E_{H_2} 0.00 volts

Q-33 The hydrogen electrode consists of platinum metal immersed in a solution which is 1 M in H^+ ions. H_2 gas at a pressure of 1 atm is bubbled over the electrode. Diagram a hydrogen electrode.

A-33

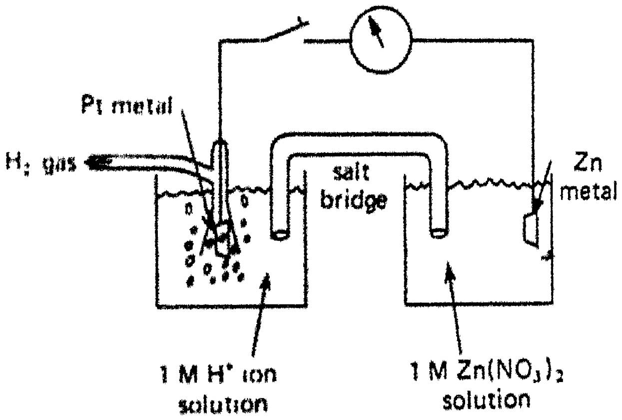


(The platinum metal serves as an aid to the transfer of electrons.)

Q-34 Diagram a cell made up of a hydrogen electrode and a zinc electrode in a 1M $Zn(NO_3)_2$ solution.

(Hint: Remember the salt bridge.)

A-34



Q-35 Represent schematically the cell from A-34. Assume the overall reaction is

$$Zn + 2H^+ \rightarrow Zn^{+2} + H_{2(g)}.$$

(Hint: The hydrogen electrode is represented as Pt, H_2(1 atm) | H^+.)

A-35 Zn | Zn^{+2}(1M) || H^+(1M) | H_2(1 atm), Pt

Q-36 In the cell represented by A-35, the emf measured is 0.762 volts. Which way do electrons flow in the external circuit?

A-36 **With the oxidation half-cell written on the left, a positive value for emf means that electrons flow from Zn to Pt.**

Q-37 What can be said about the relative ability of Zn and H_2 to be oxidized?

A-37 A positive value for the emf means that Zn has a greater tendency to be oxidized than H_2

Q-38 Represent schematically a cell which has the overall chemical reaction

$$Cu + 2H^+ \rightarrow Cu^{+2} + H_{2(g)}$$

The concentration of H^+ ions and Cu^{+2} ions in solution is 1M, and the pressure of H_2 is 1 atm

A-38 $Cu \mid Cu^{+2}(1M) \parallel H^+(1M) \mid H_2(1\ atm),\ Pt$

Q-39 In the cell represented by A-38, the emf measured is -0.345 volts. Which way do electrons flow in the external circuit?

A-39 From the Pt electrode to the Cu electrode.

Q-40 If electrons flow from Pt to Cu in the cell, write the anode and cathode reactions.

A-40 $Cu^{+2} + 2e^- \rightarrow Cu$ cathode

$H_2 \rightarrow 2H^+ + 2e^-$ anode

Q-41 What can be said about the relative ability of Cu and H_2 to be oxidized?

A-41 H_2 has a greater tendency to be oxidized.

Q-42 To actually show the reaction that takes place in the Cu-H_2 cell, which way should the reaction of Q-38 be written?

A-42 $H_{2(g)} + Cu^{+2} \rightarrow 2H^+ + Cu$

Q-43 Represent schematically a cell which has the overall chemical reaction of A-42.

A-43 $Pt,\ H_2(1\ atm) \mid H^+(1M) \parallel Cu^{+2}(1M) \mid Cu$

Q-44 Will the emf of the cell written in A-43 be positive or negative?

A-44 Since the emf of the cell written in the opposite direction was negative, reversing the reaction must change the sign of the emf. The emf would be positive.

Q-45 The voltage measured using cells that have a standard hydrogen electrode as one of their electrodes can be used to construct a table of potentials.

Oxidation reaction	$E_{(ox)}$ (volts)
$Zn \rightarrow Zn^{+2} + 2e^-$	+0 762
$Fe \rightarrow Fe^{+2} + 2e^-$	+0.440
$Sn \rightarrow Sn^{+2} + 2e^-$	+0.136
$H_2 \rightarrow 2H^+ + 2e^-$	+0.000
$Cu \rightarrow Cu^{+2} + 2e^-$	-0.345
$Ag \rightarrow Ag^+ + 1e^-$	-0.800

(For a more complete list see Table I at the end of this chapter.)

The potentials give the tendency for oxidation to take place (in a 1M solution of the ion) relative to that of hydrogen. These are called oxidation potentials. Where would the following reaction fit into the above table?

$$Al \rightarrow Al^{+3} + 3e^- = +1.67 \text{ volts}$$

A-45 The Al-Al^{+3} couple should be above the Zn-Zn^{+2} couple because the table is listed in the order of decreasing tendency to be oxidized The higher the positive value of the oxidation potential, the greater is the tendency to be oxidized

Q-46 Where would the following reaction fit into the table listed in Q-45?

$$2I^- \rightarrow I_2 + 2e^- = -0\ 535 \text{ volts}$$

A-46 The I^--I_2 couple is listed between the Cu-Cu^{+2} couple and the Ag-Ag^+ couple. A negative value means the couple is less easily oxidized than the H^+-H_2 couple

Q-47 Which is more easily oxidized, Cu or Ag metal?

A-47 Cu metal is more easily oxidized. It has a smaller negative potential

Q-48 What should be the potential of the reaction

$$Ag^+ + 1e^- \rightarrow Ag$$

relative to that of the standard hydrogen electrode?

A-48 The potential is the negative of the potential listed in the table

$$E^\circ_{Ag}(\text{ox}) = -E^\circ_{Ag}(\text{red})$$

$$E^\circ_{Ag}(\text{red}) = +0.800 \text{ volts}$$

The standard reduction potential of silver ion is 0 800 volts.

Q-49 Write the table of oxidation potentials of Q-45 in terms of reduction potentials.

A-49

reduction reaction	E°(red) (volts)
$Ag^+ + 1e^- \rightarrow Ag$	+0 800
$Cu^{+2} + 2e^- \rightarrow Cu$	+0.345
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Sn^{+2} + 2e^- \rightarrow Sn$	-0.136
$Fe^{+2} + 2e^- \rightarrow Fe$	-0 440
$Zn^{+2} + 2e^- \rightarrow Zn$	-0.762

Q-50 Which ions are more easily reduced, Cu^{+2} or Ag^+?

A-50 Ag^+ ions are more easily reduced Ag^+ has the larger $E^\circ_{(\text{red})}$ potential.

Q-51 Would a half-cell reaction which has a low tendency to undergo reduction have a high or low tendency to undergo oxidation?

A-51 high

[redacted]

S-5 The emf for a cell (two half-cells) is calculated by adding together the two standard half-cell potentials for the cell One half-cell is written as an oxidation potential, the other as a reduction potential. This is expressed mathematically as

$$E = E^\circ_{ox} + E^\circ_{red} \cdot$$

Q-52 Calculate the emf for the cell

$Zn \mid Zn^{+2}(1M) \parallel Ag^{+}(1M) \mid Ag$.

(The values for the standard electrode potential can be found in Table I.)

A-52 $E^\circ_{Zn-Zn^{+2}}$ = +0.762 volts (oxidation potential)

$E^\circ_{Ag^{+}-Ag}$ = +0.800 volts (reduction potential)

$E = E^\circ_{(ox)} + E^\circ_{(red)}$

$E = 0.762 + 0.800 = +1\ 562$ volts

Q-53 Calculate the emf for the cell

$Sn \mid Sn^{+2}(1M) \parallel Cu^{+2}(1M) \mid Cu$.

A-53 $E^\circ_{Sn-Sn^{+2}}$ = +0.136 volts (oxidation potential)

$E^\circ_{Cu^{+2}-Cu}$ = +0 345 volts (reduction potential)

$E = E^\circ_{(ox)} + E^\circ_{(red)}$

$E = 0.136 + 0.345 = +0.481$ volts

Q-54 Calculate the emf for the cell

$Fe \mid Fe^{+2}(1M) \parallel Ag^{+}(1M) \mid Ag$.

A-54 $E^\circ_{Fe-Fe^{+2}}$ = +0.440 volts (oxidation potential)

$E^\circ_{Ag^{+}-Ag}$ = +0.800 volts (reduction potential)

$E = E^\circ_{(ox)} + E^\circ_{(red)}$

$E = 0.440 + 0.800 = + 1.240$ volts

Q-55 Calculate the emf for the cell

$Ag \mid Ag^{+}(1M) \parallel Sn^{+2}(1M) \mid Sn$.

A-55 $E^\circ_{Ag-Ag^{+}}$ = -0.800 volts (oxidation potential)

$E^\circ_{Sn^{+2}-Sn}$ = -0.136 volts (reduction potential)

$E = E^\circ_{(ox)} + E^\circ_{(red)}$

$E = (-0.800) + (-0.136) = -0.936$ volts

Q-56 What does a negative emf for a cell indicate?

A-56 Electrons flow through the external circuit in the reverse direction Therefore, the opposite half-cell reactions take place spontaneously.

Q-57 The table of standard potentials can be used to predict reactions The emf of the cell is calculated from the standard potentials If the emf is positive, the reaction will occur as written If the emf is negative, the reaction will occur spontaneously in the opposite direction Will zinc metal react with a solution of Cu^{+2} ions?

A-57 $Zn \rightarrow Zn^{+2} + 2e^-$ $E^\circ_{Zn-Zn^{+2}} = +0\ 762$ volts

$Cu^{+2} + 2e^- \rightarrow Cu$ $E^\circ_{Cu^{+2}-Cu} = +0\ 345$ volts

$E = E^\circ_{(ox)} + E^\circ_{(red)}$

$E = 0.762 + 0\ 345 = +1\ 107$ volts

Yes, zinc metal will react with a solution of Cu^{+2} ions

Q-58 Could Fe metal be used to prepare H_2 gas from 1M HCl?

A-58 $Fe \rightarrow Fe^{+2} + 2e^-$ $E^\circ_{Fe-Fe^{+2}} = +0\ 440$ volts

$2H^+ + 2e^- \rightarrow H_2$ $E^\circ_{H^+-H_2} = 0\ 000$ volts

$E = E^\circ_{(ox)} + E^\circ_{(red)}$

$E = 0.440 + 0\ 000 = +0\ 440$ volts

Yes, Fe metal could be used

R a) $E = E^\circ_{(ox)} + E^\circ_{(red)}$

b) E = positive, the reaction is spontaneous as written.

c) E = negative, the reaction is spontaneous in the opposite direction.

S-6 In Chapter 7, a thermodynamic quantity called free energy change, ΔG, was shown to be related to the spontaneity of a reaction Spontaneous reactions have negative free energy changes. Therefore, there must be a relationship between the emf, E, of a cell and free energy change. This relationship is

$$\Delta G = -n\mathfrak{F}E,$$

where n is the number of electrons transferred in the reaction and $\mathfrak{F}$ is a proportionality constant equal to the number of coulombs in a faraday.

(1 faraday = 6.02 x 10^{23} electrons)

(1 coulomb = amount of electricty flowing when a current of one amp is maintained for one second)

(1 faraday = 96, 500 coulombs)

Q-59 Remembering that the relationship between free energy change and concentration was given in Chapter 7 to be

$$\Delta G = \Delta G^\circ + RT\ 2\ 3 \log \frac{[\text{product}]}{[\text{reactant}]}$$

derive a relationship between emf and concentration

(Hint· $\Delta G^\circ = -n\mathfrak{F}E^\circ$)

A-59 $\Delta G = -n\mathfrak{F}E$

$\Delta G^\circ = -n\mathfrak{F}E^\circ$

$$\Delta G = \Delta G^\circ + RT\ 2.3 \log \frac{[\text{product}]}{[\text{reactant}]}$$

$$-n\mathfrak{F}E = -n\mathfrak{F}E^\circ + RT\ 2.3 \log \frac{[\text{product}]}{[\text{reactant}]}$$

Dividing both sides of the equation by $-n\mathfrak{F}$ gives

$$E = E^\circ - \frac{RT\ 2.3}{n\mathfrak{F}} \log \frac{[\text{product}]}{[\text{reactant}]}$$

This equation is called the Nernst equation

Q-60 The Nernst equation gives the relationship between the emf of a cell and concentration. Remembering that E° is the standard electrode potential, when would $E = E^\circ$?

(Hint: $\log 1 = 0$)

A-60 When the ratio of

$$\frac{[\text{product}]}{[\text{reactant}]} = 1, \quad \log 1 = 0$$

and $E = E^\circ$

This occurs when the concentrations of the reactant and product are the same

Q-61 When measuring the standard oxidation or reduction potential, a standard state is defined where the concentration of all species in solution is 1M. The concentration of any solid is given a value of one, and the pressure of any gas is equal to 1 atm. The standard oxidation potential for hydrogen has been set equal to zero. What is the H_2 gas pressure and the H^+ ion concentration in a solution when the emf of this half-cell is equal to zero?

A-61 $H_2 \rightarrow 2H^+ + 2e^-$

$$E = E^\circ - \frac{RT\ 2.3}{n\mathfrak{F}} \log \frac{[H^+]^2}{P_{H_2}}$$

when

$P_{H_2} = 1$ atm, $[H^+] = 1M$

$E = E^\circ = 0$ volts

Q-62 When measuring the oxidation potential of Zn relative to the standard hydrogen electrode, what must be the Zn^{++} ion concentration in a solution for the measured emf to be equal to the standard oxidation potential of zinc?

A-62 $Zn \mid Zn^{+2}(?) \parallel H^+(1M) \mid H_2(1\ \text{atm})$

$E = E_{ox} + E_{red}$

$E_{red} = E^\circ_{H^+-H_2} = 0$

$E = E_{ox} = E^\circ_{Zn-Zn^{+2}}$

For the measured emf to be equal to the standard oxidation potential of Zn

$$E_{Zn-Zn^{+2}} = E^\circ_{Zn-Zn^{+2}} - \frac{RT\ 2.3}{n\mathfrak{F}} \log \frac{[Zn^{+2}]}{[Zn]}$$

$[Zn] = 1$ Defined for standard state of solid.

Therefore, if $E_{Zn-Zn^{+2}} = E^\circ_{Zn-Zn^{+2}}$, $[Zn^{+2}]$ must be 1 M.

($E_{ox} = +0.762$ volts)

Q-63 When measuring the reduction potential of silver, Ag, relative to the standard hydrogen electrode, what must the Ag^+ ion concentration be in solution for the measured emf to be equal to the standard reduction potential of silver?

A-63 $H_2(1\ atm)\ |\ H^+(1M)\ ||\ Ag^+(?)\ |\ Ag$

$E = E_{ox} + E_{red}$

$E_{ox} = E^\circ_{H_2\text{-}H^+} = 0$

$E = E_{red} = E^\circ_{Ag^+\text{-}Ag}$

For the measured emf to be equal to the standard reduction potential of silver,

$$E_{Ag^+\text{-}Ag} = E^\circ_{Ag^+\text{-}Ag} - \frac{RT\ 2\ 3}{n\mathfrak{F}} \log \frac{[Ag]}{[Ag^+]}$$

$[Ag] = 1$ Defined for standard state of solid.

Therefore, if $E_{Ag^+\text{-}Ag} = E^\circ_{Ag^+\text{-}Ag}$, $[Ag^+]$ must be equal to 1M

($E_{red} = +0.800$ volts)

Q-64 Calculate the value of the expression

$$\frac{RT(2\ 3)}{\mathfrak{F}} \text{ at } 25^\circ C$$

(R equals 8.3 joules and T must be in °K)
(1 volt = joule/coulomb)

A-64 $$\frac{2.3\ RT}{\mathfrak{F}} = \frac{(2\ 3)(8\ 3)(298^\circ)\ \text{joule}}{96,500\ \text{coulomb}}$$

$$= 0.059\ \frac{\text{joule}}{\text{coulomb}}$$

$$= 0.059 \text{ volts}$$

Q-65 For the half-cell reaction

$$Pb \rightarrow Pb^{+2} + 2e^-,$$

what value for n should be used in the Nernst equation?

A-65 n = 2

Q-66 For the half-cell reaction

$$Au^{+3} + 3e^- \rightarrow Au,$$

what value for n should be used in the Nernst equation?

A-66 n = 3

Q-67 For the $Pb \rightarrow Pb^{+2}$ half-cell reaction, what would the oxidation potential be at 25°C if the Pb^{+2} ion concentration is 0 010M?

(Hint· $E = E^\circ - \frac{0\ 059}{n} \log \frac{[\text{product}]}{[\text{reactant}]}$

$E^\circ_{Pb\text{-}Pb^{+2}} = 0\ 126$ volts)

A-67 $E^\circ_{Pb\text{-}Pb^{+2}} = 0.126$ volts

$$E = E^\circ - \frac{0.059}{n} \log \frac{[Pb^{+2}]}{[Pb]}$$

$[Pb] = 1$ $n = 2$

$$E = 0.126 - \frac{0.059}{2} \log [0.010]$$

$$E = 0.126 - (0.030)(-2.0)$$

$$= +0.19 \text{ volts}$$

Q-68 For the half-cell reaction $Au^{+3} \rightarrow Au$, what would the reduction potential be at 25°C if the Au^{+3} ion concentration is 0.10M?

$E^\circ_{Au^{+3}\text{-}Au} = +1.42$ volts

A-68 $E^\circ_{Au^{+3}-Au} = +1\ 42$ volts

$$E_{red} = E^\circ_{red} - \frac{0\ 059}{n} \log \frac{[Au]}{[Au^{+3}]}$$

$[Au] = 1 \qquad n = 3$

$$E_{red} = 1\ 42 - \frac{0\ 059}{3} \log \frac{1}{[0\ 10]}$$

$$E_{red} = 1\ 42 - 0\ 020\ (\log 10)$$

$$= +1\ 40 \text{ volts}$$

Q-69 For the Cd^{+2} - Cd half-cell reaction, what would the reduction potential be at 25°C if the Cd^{+2} ion concentration was 0 010M?

$E^\circ_{Cd^{+2}-Cd} = -0\ 402$ volts

A-69 $E^\circ_{Cd^{+2}-Cd} = -0\ 402$ volts

$$E_{red} = E^\circ - \frac{0\ 059}{n} \log \frac{[Cd]}{[Cd^{+2}]}$$

$[Cd] = 1 \qquad n = 2$

$$E_{red} = -0\ 402 - \frac{0\ 059}{2} \log \frac{1}{[0\ 010]}$$

$$E_{red} = -0\ 402 - 0\ 030(2\ 0)$$

$$= -0.462 \text{ volts}$$

Q-70 Represent schematically the cell made up of the following half-cell reactions

$Mg \rightarrow Mg^{+2}(0.010M) + 2e$

E +2.34 volts

$Sn^{+2}(0.10\ M) + 2e^- \rightarrow Sn$

E -0.136 volts

A-70 $Mg \mid Mg^{+2}\ (0.010M) \parallel Sn^{+2}\ (0.10M) \mid Sn$

Q-71 Calculate the potentials for each half-cell and the total emf at 25 C for the cell represented in A-70.

A-71 Anode

$$E_{ox} = E^\circ_{Mg-Mg^{+2}} - \frac{0\ 059}{n} \log \frac{[Mg^{+2}]}{[Mg]}$$

$$E_{ox} = 2.34 - \frac{0.059}{2} \log\ (0\ 010)$$

$$E_{ox} = 2\ 34 - 0\ 030\ (-2.0)$$

$$= +2\ 40 \text{ volts}$$

Cathode

$$E_{red} = E^\circ_{Sn^{+2}-Sn} - \frac{0.059}{n} \log \frac{[Sn]}{[Sn^{+2}]}$$

$$E_{red} = -0.136 - \frac{0.059}{2} \log \frac{1}{[0.10]}$$

$$E_{red} = -0.136 - (0\ 030)\ (1)$$

$$= -0.166 \text{ volts}$$

Cell.

$$E = E_{ox} + E_{red}$$

$$E = 2\ 40 - 0.166 = +2.23 \text{ volts}$$

Q-72 Represent schematically the cell made up of the following half-cell reactions at 25° C.

$Ni \rightarrow Ni^{+2}(0\ 10M) + 2e^-$

E +0 250 volts

$Hg^{+2}(0.10M) + 2e^- \rightarrow Hg$

E° +0.854 volts

A-72 $Ni \mid Ni^{+2}(0.10M) \parallel Hg^{+2}(0.10M) \mid Hg$

Q-73 Calculate the potential for each half-cell and the total emf at 25° C for the cell represented in A-72.

A-73 Anode

$$E_{ox} = E^\circ_{Ni-Ni^{+2}} - \frac{0.059}{n}\log\frac{[Ni^{+2}]}{[Ni]}$$

$$= 0\ 250 - \frac{0\ 059}{2}\log[0.10]$$

$$= 0\ 250 - (0\ 030)(-1.0)$$

$$= +0\ 280 \text{ volts}$$

Cathode

$$E_{red} = E^\circ_{Hg^{+2}-Hg} - \frac{0.059}{n}\log\frac{[Hg]}{[Hg^{+2}]}$$

$$= 0.854 - \frac{0\ 059}{2}\log\frac{1}{[0\ 10]}$$

$$= 0\ 854 - 0.030(1) = +0\ 824 \text{ volts}$$

Cell·

$$E = E_{ox} + E_{red}$$

$$= 0\ 28 + 0\ 824 = +1.10 \text{ volts}$$

Q-74 Calculate the potential for each half-cell and the total emf at 25°C for the cell represented schematically as

$Pb\ |\ Pb^{+2}(0\ 0010M)\ ||\ Pt,\ Cl_2(1\ atm)\ |\ Cl^-(0.10M)$.

$E^\circ_{Pb-Pb^{+2}} = +0.126$ volts

$E^\circ_{Cl_2-2Cl^-} = +1\ 358$ volts

A-74 Anode:

$$E_{ox} = E^\circ_{Pb-Pb^{+2}} - \frac{0\ 059}{n}\log\frac{[Pb^{+2}]}{[Pb]}$$

$$= +0\ 126 - \frac{0.059}{2}\log[0.0010]$$

$$= 0.126 - 0\ 030(-3\ 0)$$

$$= +0.216 \text{ volts}$$

Cathode·

$$E_{red} = E^\circ_{Cl_2-2Cl^-} - \frac{0\ 059}{n}\log\frac{[Cl^-]^2}{P_{Cl_2}}$$

$$= +1.36 - \frac{0\ 059}{2}\log[0.10]^2$$

$$= 1.36 - 0.030(-2)$$

$$= +1.42 \text{ volts}$$

Cell:

$$E = E_{ox} + E_{red}$$

$$= 0.216 + 1.42 = +1.64 \text{ volts}$$

Q-75 Calculate the potential for each half-cell and the total emf at 25°C for the cell represented schematically as

$Fe\ |\ Fe^{+3}(0.100M)\ ||\ H^+(0.010M)\ |\ Pt,\ H_2(1\ 0\ atm)$.

$E^\circ_{Fe-Fe^{+3}} = -0\ 331$ volts

A-75 Anode:

$$E_{ox} = E^\circ_{Fe-Fe^{+3}} - \frac{0.059}{n}\log\frac{[Fe^{+3}]}{[Fe]}$$

$$= -0.331 - \frac{0.059}{3}\log[0\ 100]$$

$$= -0.331 - 0.020(-1)$$

$$= -0.311 \text{ volts}$$

Cathode

$$E_{red} = E^\circ_{2H^+-H_2} - \frac{0\ 059}{n} \log \frac{P_{H_2}}{[H^+]^2}$$

$$= 0\ 00 - \frac{0\ 059}{2} \log \frac{1\ 0}{[0\ 010]^2}$$

$$= 0\ 00 - 0\ 030(4)$$

$$= -0\ 120 \text{ volts}$$

Cell

$$E = E_{ox} + E_{red}$$

$$= -0\ 311 - 0.12 = -0.43 \text{ volts}$$

Reaction goes in opposite direction

Q-76 For the cell

$Zn \mid Zn^{+2} \parallel Fe^{+2} \mid Fe$,

combine the E_{ox} and E_{red} expressions into a general expression for the emf of a cell in terms of the standard oxidation and reduction potentials and the concentration of the ions in solution

---

A-76 Anode

$$E_{ox} = E^\circ_{Zn-Zn^{+2}} - \frac{0\ 059}{n} \log \frac{[Zn^{+2}]}{[Zn]}$$

$E^\circ_{Zn-Zn^{+2}}$ = standard oxidation potential

$[Zn] = 1$ $n = 2$

Cathode

$$E_{red} = E^\circ_{Fe^{+2}-Fe} - \frac{0.059}{n} \log \frac{[Fe]}{[Fe^{+2}]}$$

$E^\circ_{Fe^{+2}-Fe}$ = standard reduction potential

$[Fe] = 1$ $n = 2$

Cell

$$E = E_{ox} + E_{red}$$

$$E = E^\circ_{Zn-Zn^{+2}} - \frac{0.059}{n} \log [Zn^{+2}] + E^\circ_{Fe^{+2}-Fe} - \frac{0.059}{n} \log \frac{1}{[Fe^{+2}]}$$

$$E = E^\circ_{Zn-Zn^{+2}} + E^\circ_{Fe^{+2}-Fe} - \frac{0.059}{n} \log \frac{[Zn^{+2}]}{[Fe^{+2}]}$$

Q-77 Write the cell reaction taking place in Q-76.

A-77 $Zn + Fe^{+2} \rightarrow Zn^{+2} + Fe$

Q-78 Write the equilibrium expression for the reaction in A-77.

A-78 $K_{eq} = \frac{[Zn^{+2}]}{[Fe^{+2}]}$

Q-79 From your knowledge that ΔG is equal to zero when a reaction is at equilibrium and the relationship between ΔG and emf of a cell (S-6), calculate the cell potential when the ions in solution are at equilibrium.

A-79 $\Delta G = -n\mathfrak{F}E$. At equilibrium $\Delta G = 0$.

$0 = -n\mathfrak{F}E$

Therefore, $E = 0$ at equilibrium.

Q-80 Using the equations from A-76 and A-78 and the knowledge that E is zero at equilibrium, derive an expression for the relationship between standard electrode potentials and K_{eq}.

A-80

$$E = E^\circ_{Zn-Zn^{+2}} + E^\circ_{Fe^{+2}-Fe} - \frac{0.059}{n} \log \frac{[Zn^{+2}]}{[Fe^{+2}]}$$

$$E = 0 \quad \text{when} \quad \frac{[Zn^{+2}]}{[Fe^{+2}]} = K_{eq}$$

Therefore,

$$E^\circ_{Zn-Zn^{+2}} + E^\circ_{Fe^{+2}-Fe} = \frac{0.059}{n} \log K_{eq}$$

Q-81 Use the equation derived in A-76 to obtain a general expression for the emf of a cell in terms of E°_{ox}, E°_{red}, [products] and [reactants]

A-81

$$E = E^\circ_{Zn-Zn^{+2}} + E^\circ_{Fe^{+2}-Fe} - \frac{0.059}{n} \log \frac{[Zn^{+2}]}{[Fe^{+2}]}$$

$$E^\circ_{Zn-Zn^{+2}} = E^\circ_{ox}$$

$$E^\circ_{Fe^{+2}\ Fe} = E^\circ_{red}$$

$$[Zn^{+2}] = [\text{products}]$$

$$[Fe^{+2}] = [\text{reactants}]$$

Therefore,

$$E = E^\circ_{ox} + E^\circ_{red} - \frac{0.059}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

Q-82 Using the expression obtained in A-81, derive an equation for the relationship between E°_{ox}, E°_{red} and K_{eq}.

(Hint· What is E at equilibrium?)

A-82

$$E = 0 \text{ when } \frac{[\text{products}]}{[\text{reactants}]} = K_{eq}$$

Therefore,

$$E^\circ_{ox} + E^\circ_{red} = \frac{0.059}{n} \log K_{eq}$$

Q-83 Calculate K_{eq} for the reaction of Zn with Fe^{+2}

A-83

$$\log K_{eq} = \frac{E^\circ_{Zn-Zn^{+2}} + E^\circ_{Fe^{+2}-Fe}}{\frac{0.059}{n}}$$

$$= \frac{0.32}{0.030} = 11$$

$$K_{eq} = \text{antilog } 11 = 1 \times 10^{11}$$

Q-84 What does the large value of K_{eq} in A-83 tell about the reaction?

A-84 This large value of K_{eq} means that the reaction goes practically to completion.

Q-85 Calculate K_{eq} for the reaction

$$Sn + Pb^{+2} \rightarrow Sn^{+2} + Pb$$

$$E^\circ_{Sn-Sn^{+2}} = 0.136 \text{ volts}$$

$$E^\circ_{Pb^{+2}-Pb} = -0.126 \text{ volts}$$

A-85 Half-reactions

$Sn \rightarrow Sn^{+2} + 2e^-$ $\quad E^\circ = 0.136$

$Pb^{+2} + 2e^- \rightarrow Pb$ $\quad E^\circ = -0.126$

$$E^\circ_{ox} + E^\circ_{red} = 0.136 - 0.126 = +0.010 \text{ volts}$$

$$E^\circ_{ox} + E^\circ_{red} = \frac{0.059}{n} \log K_{eq}$$

$$\log K_{eq} = \frac{0.010}{0.059/2} = 0.33$$

$$K_{eq} = 2.1$$

Q-86 Calculate K_{eq} for the reaction

$$Cd + 2Ag^+ \rightarrow 2Ag + Cd^{+2}$$

(Hint The half-cell for silver is written as $2Ag^+ + 2e^- \rightarrow 2Ag$ so that the value of n for silver and Cd will be identical This doesn't change the E° value for the silver half-cell.)

$E^\circ_{Cd-Cd^{+2}} = 0.402$ volts

$E^\circ_{Ag^+-Ag} = 0.7995$ volts

A-86 Half-reactions

$Cd \rightarrow Cd^{+2} + 2e^-$ $\quad E^\circ = 0.402$ volts

$2Ag^+ + 2e^- \rightarrow Ag$ $\quad E^\circ = 0.7995$ volts

$$E^\circ_{ox} + E^\circ_{red} = 0.402 + 0.800 = +1.202 \text{ volts}$$

$$E^\circ_{ox} + E^\circ_{red} = \frac{0.059}{n} \log K_{eq}$$

$$\log K_{eq} = \frac{1.202}{0.059/2} = 40$$

$$K_{eq} = 10^{40}$$

Remember, $K_{eq} = \dfrac{[Cd^{+2}]}{[Ag^+]^2}$

Q-87 Show that the E of the half-cell for silver will be identical whether the half-cell is written with one electron transferred or two electrons transferred.

$$Ag^+ + e^- \rightarrow Ag$$

$$2Ag^+ + 2e^- \rightarrow 2Ag$$

(Hint: $2 \log x = \log x^2$ and $\log \frac{1}{x^2} = \log x^{-2} = -2 \log x$).

A-87 For $Ag^+ + e^- \rightarrow Ag$

$$E' = E^\circ_{Ag^+-Ag} - \frac{0.059}{n} \log \frac{1}{[Ag^+]}$$

$n = 1$

$$E' = E^\circ_{Ag^+-Ag} - \frac{0.059}{1} \log [Ag^+]^{-1}$$

$$E' = E^\circ_{Ag^+-Ag} - \frac{0.059}{\cancel{1}} (-\cancel{1}) \log [Ag^+]$$

$$E' = E^\circ_{Ag^+-Ag} + 0.059 \log [Ag^+]$$

For $2Ag^+ + 2e^- \rightarrow 2Ag$

$$E = E^\circ_{2Ag^+-2Ag} - \frac{0.059}{n} \log \frac{1}{[Ag^+]^2}$$

$n = 2$

$$E = E^\circ_{2Ag^+-2Ag} - \frac{0.059}{2} \log [Ag^+]^{-2}$$

$$E = E^\circ_{2Ag^+-2Ag} - \frac{0.059}{\cancel{2}} (-\cancel{2}) \log [Ag^+]$$

$$E = E^\circ_{2Ag^+-2Ag} + 0.059 \log [Ag^+]$$

Therefore, since

$$E^\circ_{Ag^+-Ag} \equiv E^\circ_{2Ag^+-2Ag}$$

$$E' = E$$

Q-88 Calculate K_{eq} for the reaction

$$2Cr + 3Fe^{+2} \rightarrow 2Cr^{+3} + 3Fe.$$

$$K_{eq} = \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3}$$

$E^\circ_{Cr-Cr^{+3}} = 0.71$ volts

$E^\circ_{Fe^{+2}-Fe} = -0.44$ volts

A-88 Half-reactions

$2Cr \rightarrow 2Cr^{+3} + 6e^- \quad E^\circ = 0.71$ volts

$3Fe^{+2} + 6e^- \rightarrow 3Fe \quad E^\circ = -0.44$ volts

$n = 6$

$$E^\circ_{ox} + E^\circ_{red} = 0.71 - 0.44$$
$$= +0.27 \text{ volts}$$

$$K_{eq} = \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3}$$

$$E^\circ_{ox} + E^\circ_{red} = \frac{0.059}{n} \log K_{eq}$$

$$\log K_{eq} = \frac{0.27}{0.059/6} = 27$$

$$K_{eq} = 10^{27}$$

Q-89 What does this large value of K_{eq} tell about the reaction?

A-89 The reaction goes essentially to completion before equilibrium is reached

Q-90 Cr metal is placed in a solution with $[Fe^{+2}] = 1.0 \times 10^{-3}$ mole/liter and $[Cr^{+3}] = 0.20$ mole/liter. Express $[Fe^{+2}]$ at equilibrium in terms of $[Cr^{+3}]$ at equilibrium. ($K_{eq} = 10^{27}$)

A-90
$$K_{eq} = \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3} = 10^{27}$$

Therefore, at equilibrium

$$[Fe^{+2}] = \sqrt[3]{\frac{[Cr^{+3}]^2}{10^{27}}}$$

Q-91 For the reaction described in Q-90, write an expression for the $[Cr^{+3}]$

(Hint: Let x = concentration of Cr^{+3} formed in the reaction.)

A-91 $[Cr^{+3}] = 0.20$ mole/liter + x where x is the concentration of Cr^{+3} formed in the reaction.

Q-92 For the reaction described in Q-90, will the concentration x be significant compared to the original $[Cr^{+3}]$ which equals 0.20M?

A-92 If <u>all</u> the Fe^{+2} is reduced only 2/3 of 0.0010 moles of Cr^{+3} will be produced. Since this maximum concentration of Cr^{+3}(0.00066M) from the reaction is much smaller than the original concentration of Cr^{+3}(0.20M), it can be neglected.

Q-93 For the reaction described in Q-90, calculate the equilibrium concentration of Fe^{+2} using the approximation that $[Cr^{+3}] = 0.20M$

A-93
$$[Fe^{+2}]^3 = \frac{[Cr^{+3}]^2}{K_{eq}}$$

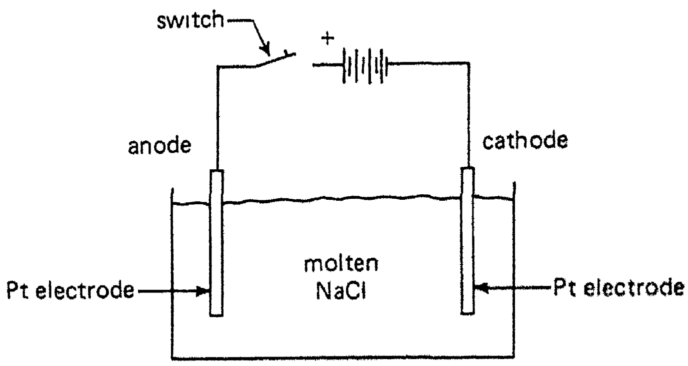
$$[Fe^{+2}] = \sqrt[3]{\frac{(0.20)^2}{10^{27}}} = \sqrt[3]{4.0 \times 10^{-29}}$$

$$[Fe^{+2}] = 3.4 \times 10^{-10} \text{ M}$$

[redacted]

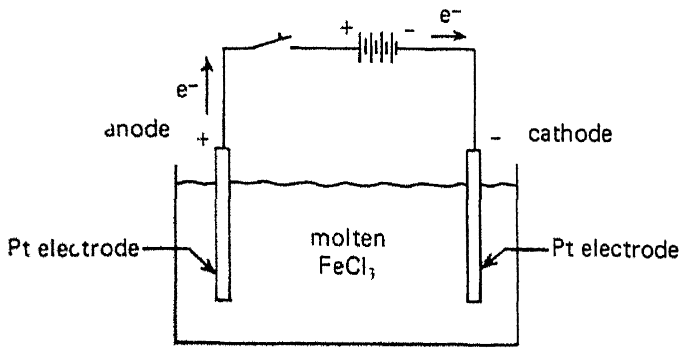
PART II: Electrolytic Cells and Faraday's Law

S-1 Electrical energy can be converted into chemical energy by using a battery in the external circuit of a cell to act as an electron pump. This type of cell is called an electrolytic cell, and the process of using an electric current to produce a chemical reaction is called electrolysis. The electrolysis of molten sodium chloride can be accomplished by the electrolytic cell illustrated. Molten sodium chloride is composed of mobile Na^+ and Cl^- ions.



	Q-1 The symbol + ⊣⊢ - is used to represent a battery (the electron pump). Electrons are pushed from the negative pole of the battery to the electrode. Will the cathode or anode be the negative electrode in an electrolytic cell?
A-1 Electrons are being pumped to the cathode making this the negative electrode	Q-2 What will be the polarity of the anode? Why?
A-2 Positive. The electron pump pulls electrons away from this electrode.	Q-3 The Na^+ ions will migrate to the negative cathode. What reaction will take place at this electrode? Is it oxidation or reduction?
A-3 $Na^+ + e^- \rightarrow Na$ reduction	Q-4 The Cl^- ions will migrate to the positive anode. What reaction will take place at this electrode? Is it oxidation or reduction?
A-4 $2Cl^- \rightarrow Cl_2 + 2e^-$ oxidation	Q-5 Diagram a cell for the electrolysis of molten $FeCl_3$. Show the anode and cathode reactions, the flow of electrons through the external circuit, and the polarity of the electrodes.

A-5



Cathode reaction $Fe^{+3} + 3e^- \rightarrow Fe$ (reduction)

Anode reaction $2Cl^- \rightarrow Cl_2 + 2e^-$ (oxidation)

R

a) An electrolytic cell converts electrical energy into chemical energy.

b) Reduction occurs at the cathode which is negatively charged.

c) Oxidation occurs at the anode which is positively charged.

S-2 Electrolysis of aqueous solutions is more complicated Water molecules, as well as the ions of the dissolved electrolyte, are present and may be oxidized or reduced according to the following reactions.

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ cathode reaction

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ anode reaction

In the electrolysis of aqueous solutions of ions, the reactions occurring at the electrodes are the reactions that have the highest E° values

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Q-6 Write the possible cathode reactions which could occur at an inert electrode (e.g , Pt metal) in the electrolysis of aqueous NaBr

A-6 1) $Na^+ + e^- \rightarrow Na$

2) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Q-7 The E°_{red} value for H_2O is larger than that for Na Which reaction will occur at the cathode in the electrolysis of a NaBr solution?

A-7 H_2O is more easily reduced than Na^+ (E°_{red} larger value) so reaction 2 occurs.

Q-8 In general, if the cation of the electrolyte is an alkali or alkaline earth metal, H_2 gas is liberated at the cathode What is the cathode reaction in the electrolysis of an aqueous solution of KNO_3?

A-8 $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

K is an alkali metal.

Q-9 What is the cathode reaction for the electrolysis of an aqueous solution of $CuSO_4$? (Hint. Refer to Table I, page 423)

A-9 $Cu^{+2} + 2e^- \rightarrow Cu$

E°_{red} of Cu^{+2} is larger than that of H_2O

Q-10 Write the possible anode reactions which could occur at an inert electrode in the electrolysis of aqueous NaBr

A-10 1) $2Br^- \rightarrow Br_2 + 2e^-$

2) $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Q-11 The E°_{ox} value for Br^- is larger than that for H_2O Which reaction will occur at the anode in the electrolysis of a NaBr solution?

A-11 Br^- is more easily oxidized than H_2O (E°_{ox} larger value) so reaction 1 occurs. Br^- and I^- are both more easily oxidized than H_2O

Q-12 Write the anode reaction for the electrolysis of KI

A-12 $2I^- \rightarrow I_2 + 2e^-$

Q-13 If the anode is not an inert metal, the metal goes into solution and electrons are passed along in the wire conductor. What would be the anode reaction if the anode were silver metal?

A-13 $Ag \rightarrow Ag^+ + e^-$

Q-14 Molten $CaCl_2$ is electrolyzed with inert carbon electrodes. What is the cathode reaction?

A-14 $Ca^{+2} + 2e^- \rightarrow Ca$

Q-15 What is the anode reaction for the electrolysis cell described in Q-14?

A-15 $2Cl^- \rightarrow Cl_2 + 2e^-$

Q-16 An aqueous $FeSO_4$ solution is electrolyzed with inert platinum electrodes. What are the cathode and anode reactions?

(Hint. In general, if the anion contains oxygen, e.g., NO_3^-, SO_4^{-2}, H_2O is oxidized at the anode.)

A-16 Cathode:

$$Fe^{+2} + 2e^- \rightarrow Fe$$

Anode

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Q-17 An aqueous $CuSO_4$ solution is electrolyzed with copper electrodes. What are the cathode and anode reactions?

A-17 Cathode

$$Cu^{+2} + 2e^- \rightarrow Cu$$

Anode:

$$Cu \rightarrow Cu^{+2} + 2e^-$$

R In the electrolysis of aqueous solutions of ions, the reactions occurring at the electrodes are the reactions that have the highest E° values.

S-3 The amount of material undergoing chemical change at an electrode is proportional to the quantity of electricity (Q) flowing through the cell

$$Q = It$$

(I is the current in amperes (coulombs/sec) and t is the time)

and to the gram-equivalent weight of the substance

$$\text{g-eq wt} = \frac{\text{atomic weight}}{n}$$

(n is the number of electrons transferred)

The foregoing statements are the basis of Faraday's law.

Q-18 In the reaction

$$Na^+ + e^- \rightarrow Na,$$

what is the gram-equivalent weight of Na?

A-18 g-eq $\frac{23.0}{1} = 23.0$ g

Q-19 In the reaction

$$Cu^{+2} + 2e^- \rightarrow Cu,$$

what is the gram-equivalent weight of Cu?

A-19 g-eq $\frac{63.5}{2}$ 31.8 g

Q-20 In the reaction

$$Al^{+3} + 3e^- \rightarrow Al,$$

what is the gram-equivalent weight of Al?

A-20 g-eq $\frac{27.0}{3}$ 9.0 g

Q-21 How many electrons would be required to reduce one gram-equivalent of Na^+ to Na metal?

A-21 6.02×10^{23} electrons

Q-22 How many electrons would be required to reduce one gram-equivalent of Al^{+3} to Al metal?

A-22 6.02×10^{23} electrons

Q-23 How many electrons would be required to reduce one gram-equivalent of any metal ion to the metal?

A-23 6.02×10^{23} electrons

This number of electrons is given a special name called the faraday.

Q-24 The faraday is the electrical charge on one mole of electrons. Calculate the value of the faraday, $\mathfrak{F}$, in coulombs

(Hint: The charge of an electron is 1.60×10^{-19} coulombs/electron.)

A-24 $$\mathfrak{F} = \frac{6.02 \times 10^{23}\ \cancel{\text{electron}}}{\text{mole of electron}} \left| \frac{1.60 \times 10^{-19}\ \text{coulomb}}{\cancel{\text{electron}}} \right.$$

96,300 coulomb/mole of electron

The accepted value for the faraday is 96,500 coulomb/mole. This value is obtained by using four significant figures, i.e.,

$$\frac{6.023 \times 10^{23}\ \cancel{\text{electron}}}{\text{mole}} \left| \frac{1.602 \times 10^{-19}\ \text{coulomb}}{\cancel{\text{electron}}} \right.$$

96,500 coulomb/mole

Q-25 How many faradays are needed to reduce one gram-equivalent of any element?

A-25 1 faraday

$\mathfrak{F} = 96{,}500$ coulomb/g-eq of element

Q-26 How many faradays are needed to reduce 4 gram-equivalents of Cu^{+2} to Cu metal?

A-26 $$\frac{4\ \cancel{\text{g-eq}}}{} \left| \frac{1\mathfrak{F}}{1\ \cancel{\text{g-eq}}} \right. = 4\mathfrak{F}$$

Q-27 If 5.00 faradays of current were passed through molten sodium chloride, what mass of Na metal would be deposited?

A-27 $$\frac{5\ 00\,\cancel{\mathcal{F}}}{} \times \frac{1\,\cancel{\text{g-eq}}}{1\,\cancel{\mathcal{F}}} \times \frac{23\ 0 \text{ g of Na}}{1\,\cancel{\text{g-eq}}\text{ of Na}} = 115 \text{ g}$$

Q-28 If 4 0 faradays of current were passed through an aqueous solution of Al^{+3} ions, what mass of Al metal would be deposited on the electrode?

A-28 $$\frac{4.0\,\cancel{\mathcal{F}}}{} \times \frac{1\,\cancel{\text{g-eq}}}{1\,\cancel{\mathcal{F}}} \times \frac{\frac{27}{3}\text{ g of Al}}{1\,\cancel{\text{g-eq}}\text{ of Al}} = 36 \text{ g of Al}$$

Q-29 If 193,000 coulomb were passed through a cell containing one liter of aqueous solution of 5M Cu^{+2} ions, what mass of Cu metal would be deposited on the electrode?

A-29 $$\frac{193{,}000\,\cancel{\text{coulomb}}}{} \times \frac{1\,\cancel{\mathcal{F}}}{96{,}500\,\cancel{\text{coulomb}}} \times \frac{1\,\cancel{\text{g-eq}}}{1\,\cancel{\mathcal{F}}} \times \frac{\frac{63.5}{2}\text{ g of Cu}}{1\,\cancel{\text{g-eq}}\text{ of Cu}} = 63.5 \text{ g of Cu}$$

Q-30 If a current of 5 0 amps is passed through a cell for 2 0 hours, what <u>quantity</u> of electricity is passed through the cell?

A-30 $$\frac{2\ 0\,\cancel{\text{hr}}}{} \times \frac{60\,\cancel{\text{min}}}{1\,\cancel{\text{hr}}} \times \frac{60 \text{ sec}}{1\,\cancel{\text{min}}} = 7200 \text{ sec}$$

$$Q = It = \frac{5\ 0 \text{ coulomb}}{\cancel{\text{sec}}} \times \frac{7200\,\cancel{\text{sec}}}{}$$

$$= 3\ 6 \times 10^4 \text{ coulomb}$$

Q-31 How many grams of Al would be deposited on the electrode using a quantity of electricity equal to that of Q-30?

A-31 $$\frac{3.6 \times 10^4\,\cancel{\text{coulomb}}}{} \times \frac{1\,\cancel{\mathcal{F}}}{96{,}500\,\cancel{\text{coulomb}}} \times \frac{1\,\cancel{\text{g-eq}}}{1\,\cancel{\mathcal{F}}} \times \frac{\frac{27.0}{3}\text{ g of Al}}{1\,\cancel{\text{g-eq}}\text{ of Al}} \quad 3.4 \text{ g of Al}$$

Q-32 If a current of 10 amps is passed for two hours through a cell containing 1000 g molten NaCl, what mass of Na metal would be deposited on the electrode?

A-32 First, convert hours to seconds.

$$\frac{2\,\cancel{\text{hr}}}{} \times \frac{60\,\cancel{\text{min}}}{1\,\cancel{\text{hr}}} \times \frac{60 \text{ sec}}{1\,\cancel{\text{min}}} = 7200 \text{ sec}$$

The number of coulombs is

$$Q = It$$

$$= 10 \text{ coulomb}/\cancel{\text{sec}}\ (7200\,\cancel{\text{sec}})$$

$$= 72{,}000 \text{ coulomb}$$

$$\frac{72{,}000\,\cancel{\text{coulomb}}}{} \times \frac{1\,\cancel{\mathcal{F}}}{96{,}500\,\cancel{\text{coulomb}}} \times \frac{1\,\cancel{\text{g-eq}}}{1\,\cancel{\mathcal{F}}} \times \frac{23.0 \text{ g of Na}}{1\,\cancel{\text{g-eq}}\text{ of Na}} = 17 \text{ g of Na}$$

Q-33 A current of ten amps is passed through 1000 g of molten $MgCl_2$ for 15 minutes (inert electrodes). Write the equations for the reactions that occur at the electrodes.

A-33 Cathode

$Mg^{+2} + 2e^- \rightarrow Mg$

Anode

$2Cl^- \rightarrow Cl_2 + 2e^-$

Q-34 What mass of Mg metal would be deposited at the cathode if the electrolysis described in Q-33 is carried out?

A-34 $Q = \frac{10 \text{ coulomb}}{\cancel{\text{sec}}} \bigg| \frac{60 \cancel{\text{sec}}}{\cancel{\text{min}}} \bigg| \frac{15 \cancel{\text{min}}}{} = 9000 \text{ coulomb}$

$$\frac{9000 \cancel{\text{coulomb}}}{} \bigg| \frac{1\cancel{\mathcal{F}}}{96{,}500 \cancel{\text{coulomb}}} \bigg| \frac{1 \cancel{\text{g-eq}}}{1\cancel{\mathcal{F}}} \bigg| \frac{\frac{24}{2} \text{ g of Mg}}{1 \cancel{\text{g-eq}} \text{ of Mg}} = 1\ 13 \text{ g of Mg}$$

Q-35 For the electrolysis described in Q-33, what mass of Cl_2 gas would be liberated at the anode?

A-35

$$\frac{9000 \cancel{\text{coulomb}}}{} \bigg| \frac{1\cancel{\mathcal{F}}}{96{,}500 \cancel{\text{coulomb}}} \bigg| \frac{1 \cancel{\text{g-eq}}}{1\cancel{\mathcal{F}}} \bigg| \frac{\frac{71}{2} \text{ g of } Cl_2}{1 \cancel{\text{g-eq}} \text{ of } Cl_2} = 3\ 3 \text{ g of } Cl_2$$

Q-36 For the electrolysis described in Q-33, what volume of Cl_2 gas is liberated at standard conditions?
(R = 0 082 liter-atm/deg-mole)

A-36 PV = nRT (n = number of moles)

$$V = \frac{nRT}{P}$$

$$V = \frac{\left(\frac{3.3 \cancel{\text{g}}}{71 \cancel{\text{g/mole}}}\right)\left(0\ 082 \frac{\text{liter-}\cancel{\text{atm}}}{\cancel{\text{mole-deg}}}\right)\left(273 \cancel{\text{deg}}\right)}{1 \cancel{\text{atm}}} = 1.0 \text{ liter}$$

Q-37 A quantity of electricity equal to 4 003 $\mathcal{F}$ is needed to plate out a given amount of metal If a current of 5 00 amp is used in the cell, how long (in hr) will it take to plate out the metal?

A-37 $\frac{4.003\cancel{\mathcal{F}}}{} \bigg| \frac{96{,}500 \text{ coulomb}}{1\cancel{\mathcal{F}}}$

$= 386{,}000 \text{ coulomb}$

$Q = It \qquad t = \frac{Q}{I}$

$$t = \frac{386{,}000 \cancel{\text{coulomb}}}{5.00 \cancel{\text{coulomb}}/\text{sec}} = 77{,}200 \text{ sec}$$

$$\frac{77{,}200 \cancel{\text{sec}}}{} \bigg| \frac{1 \cancel{\text{min}}}{60 \cancel{\text{sec}}} \bigg| \frac{1 \text{ hr}}{60 \cancel{\text{min}}} = 21\ 4 \text{ hr}$$

Q-38 An aqueous $CdSO_4$ solution is electrolyzed Write the equations for the reactions that occur at the electrodes.

A-38 Cathode:

$Cd^{+2} + 2e^- \rightarrow Cd$

Anode:

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Q-39 How long would it take to deposit 2.00 g of Cd if a current of 0 250 amp is used?

A-39 $\dfrac{2.00\,\cancel{\text{g of Cd}}}{} \left| \dfrac{1\,\cancel{\text{g-eq}}}{\frac{112}{2}\,\cancel{\text{g of Cd}}} \right| \dfrac{1\cancel{\mathcal{F}}}{1\,\cancel{\text{g-eq}}} \left| \dfrac{96{,}500 \text{ coulomb}}{1\cancel{\mathcal{F}}} \right. = 3\ 45 \times 10^3 \text{ coulomb}$

$Q = It \qquad t = \dfrac{Q}{I}$

$t = \dfrac{3.45 \times 10^3\,\cancel{\text{coulomb}}}{0\ 250\,\cancel{\text{coulomb}}/\text{sec}} = 1\ 38 \times 10^4 \text{ sec}$

$\dfrac{1\ 38 \times 10^4\,\cancel{\text{sec}}}{} \left| \dfrac{1 \text{ hr}}{3\ 60 \times 10^3\,\cancel{\text{sec}}} \right. = 3\ 83 \text{ hr}$

Q-40 An aqueous solution of $CdSO_4$ is electrolyzed and 2 00 g of Cd is deposited What volume of O_2 at STP would be liberated at the anode?

A-40 $\dfrac{3.45 \times 10^3\,\cancel{\text{coulomb}}}{} \left| \dfrac{1\cancel{\mathcal{F}}}{96{,}500\,\cancel{\text{coulomb}}} \right| \dfrac{1\,\cancel{\text{g-eq}}}{1\cancel{\mathcal{F}}} \left| \dfrac{\frac{32\ 0}{4}\,\cancel{\text{g of } O_2}}{1\,\cancel{\text{g-eq of } O_2}} \right| \dfrac{1\,\cancel{\text{mole}}}{32\ 0\,\cancel{\text{g of } O_2}} \left| \dfrac{22\ 4 \text{ liter}}{1\,\cancel{\text{mole}}} \right.$

$= 0\ 200$ liter

R

a) $Q = It$

b) Gram-equivalent weight

$$= \frac{\text{atomic weight}}{n}$$

where n is the number of electrons transferred.

c) One faraday of electricity will plate out one gram-equivalent of any element.

d) $\mathcal{F}$ = 96,500 coulomb

= 1 mole of electrons

PART III: Oxidation Potentials

S-1 Oxidation potentials measure the tendency of a substance to be oxidized in aqueous solution. The larger the potential, the more easily the substance is oxidized. Ionization energy is the energy necessary to remove an electron from an atom in the gas phase The higher the ionization energy, the more difficult it is to remove the electron.

$K_{(s)} \rightleftharpoons K^+_{(aq)} + e^-$ oxidation potential = 2.92 volts

$K_{(g)} \rightleftharpoons K^+_{(g)} + e^-$ ionization energy = 100.1 kcal/mole

Element	Oxidation Potential (volts)	Ionization Energy (kcal/mole)
Li	+3.02	124.3
Na	+2.71	118.5
K	+2.92	100.1
Rb	+2.93	96.31
Cs	+2.92	89.78

	Q-1 Will the tendency for the following reaction to occur be measured by ionization energy or oxidation potential? $M_{(g)} \rightleftarrows M^+_{(g)} + e^-$
A-1 Ionization energy The substance is in the gas phase.	Q-2 A galvanic cell is constructed from copper and silver electrodes, $CuSO_4$ and $AgNO_3$ solutions, and a salt bridge. If the potential of the cell is to be calculated, should a table of ionization energies or oxidation potentials be consulted? Why?
A-2 Table of oxidation potentials The reactions would occur between solid metals and an aqueous solution of ions	Q-3 According to the table given in S-1, which solid metal will oxidize to form an ion in solution most easily?
A-3 Li has the largest oxidation potential	Q-4 According to the table given in S-1 which gaseous metal will lose an electron and form a gaseous ion most easily?
A-4 Cs, because it has the lowest ionization energy	Q-5 According to the table, which metal in the gaseous state has the <u>least</u> tendency to lose an electron? Is this metal also the most difficult to oxidize to give ions in aqueous solutions?
A-5 Li has the least tendency to lose an electron in the gas phase On the other hand, Li has the highest oxidation potential which means it is the most easily oxidized to give ions in aqueous solution.	Q-6 The apparent contradiction indicated in the preceding answer may be explained by analysis of the following reactions. $Li_{(s)} \rightarrow Li_{(g)}$ (1) $Li_{(g)} \rightarrow Li^+_{(g)} + e^-$ (2) $Li^+_{(g)} + H_2O \rightarrow Li^+_{(aq)}$ (3) Add the three reactions What process does the resultant reaction describe?
A-6 $Li_{(s)} + H_2O \rightarrow Li^+_{(aq)} + e^-$ Oxidation of solid Li to give ions in solution.	Q-7 For the reaction given in A-6, will ionization energy or oxidation potential measure the tendency for the ion to form?
A-7 Oxidation potential. A solid is oxidized to an ion in solution.	Q-8 Is the energy required for any of the reactions listed in Q-6 measured by ionization energy? Which one?
A-8 Yes, reaction (2). The energy required to remove an electron from a gaseous atom is the ionization energy.	Q-9 Sublimation energy is defined as the energy necessary to convert a solid to a gas Which reaction of those given in Q-6 represents sublimation?

A-9 Reaction (1) is the conversion of solid Li to gaseous Li

Q-10 When a gaseous ion dissolves in water, energy is released, this energy is called hydration energy What three energy terms are included in the oxidation potential?

A-10 The sublimation energy, ionization energy of the gaseous atom and the hydration energy

Q-11 If the ionization energy and hydration energy of two atoms were the same, would the atom with the higher sublimation energy have the higher or lower oxidation potential? Why?

A-11 Lower oxidation potential. More energy would be required to sublime the atom with the higher sublimation energy, therefore, this atom would be more difficult to oxidize (lower oxidation potential)

Q-12 If the sublimation and hydration energies of two atoms were the same, would the atom with the higher ionization energy have the higher or lower oxidation potential? Why?

A-12 Lower oxidation potential. More energy is required to remove an electron from the gaseous atom with the higher ionization energy; therefore, this atom would be more difficult to oxidize

Q-13 If the sublimation energy and ionization energy of two atoms were the same, would the atom with the higher hydration energy have the higher or lower oxidation potential?

A-13 Higher oxidation potential More energy is released when the ion with the larger hydration energy is dissolved in water, therefore, the atom would be easier to oxidize.

Q-14 The sublimation energy for Na is less than that for Li. The ionization energy for Na is slightly less than that for Li. However, the oxidation potential for Li is greater than for Na. How can this be explained?

A-14 The hydration energy for Li is much greater than for Na. The hydration energy is large enough to be the determining factor.

Q-15 Ionization energies of the elements show well defined trends. Oxidation potentials of the elements, on the other hand, exhibit only a few well defined trends. How can this difference be accounted for?

A-15 Oxidation potentials are dependent upon three energy factors while the ionization energy is dependent upon a single energy term.

[redacted]

PART IV: Balancing Oxidation – Reduction Equations

S-1 In Chapter 2, oxidation-reduction equations were balanced by the "change in oxidation state" method. A second way of balancing oxidation-reduction (redox) equations, called the "half-reaction" method, will now be demonstrated. The next several S- statements will be used to present the six steps necessary to balance redox equations by the "half-reaction" method. After mastering these operations, any chemical equation can be balanced by combining the six steps.

Every redox equation may be conveniently divided into an oxidation and a reduction half-reaction. These half-reactions are the reactions which occur at the electrodes in an electrochemical process. Each half-reaction can be balanced separately. For example,

Reaction	$Fe^{+2} + MnO_4^- \rightarrow Fe^{+3} + Mn^{+2}$
Oxidation half-reaction	$Fe^{+2} \rightarrow Fe^{+3} + e^-$
Reduction half-reaction	$5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$

Q-1 Separate the following reaction into an oxidation and a reduction half-reaction. Do not attempt to balance the reactions. Do not add electrons

$$Cu^+ + Ag \rightarrow Cu + Ag^+$$

A-1 $Cu^+ \rightarrow Cu$

$Ag \rightarrow Ag^+$

Q-2 Separate the following reaction into an oxidation and a reduction half-reaction. Do not attempt to balance the reactions. Do not add electrons.

$$NO_2^- + Cr_2O_7^{-2} \rightarrow NO_3^- + Cr^{+3}$$

A-2 $NO_2^- \rightarrow NO_3^-$

$Cr_2O_7^{-2} \rightarrow Cr^{+3}$

Q-3 Separate the following reaction into an oxidation and a reduction half-reaction. Do not attempt to balance the reactions. Do not add electrons

$$H_2S + HNO_3 \rightarrow S + NO$$

A-3 $H_2S \rightarrow S$

$HNO_3 \rightarrow NO$

Q-4 Separate the following reaction into an oxidation and a reduction half-reaction. Do not attempt to balance the half-reactions. Do not add electrons.

$$ClO_3^- \rightarrow ClO_4^- + ClO_2$$

A-4 $ClO_3^- \rightarrow ClO_4^-$

$ClO_3^- \rightarrow ClO_2$

Q-5 For the following reaction, write the appropriate half-reactions. Include in the half-reactions only those species undergoing oxidation or reduction. Do not add electrons or attempt to balance the half-reactions.

$$H_3AsO_4 + H_2S \rightarrow H_3AsO_3 + S + H_2O$$

A-5 $H_3AsO_4 \rightarrow H_3AsO_3$

$H_2S \rightarrow S$

Q-6 Divide the following reaction into the appropriate half-reactions, including only the species which undergo an oxidation or reduction Do not balance the equations or add electrons

$$Mn^{+2} + BiO_3^- \rightarrow MnO_4^- + Bi^{+3}$$

A-6 $Mn^{+2} \rightarrow MnO_4^-$

$BiO_3^- \rightarrow Bi^{+3}$

R **The first step in balancing redox equations by the "half-reaction" method is to divide the equation into the appropriate half-reactions. Only species which undergo oxidation or reduction are included in the half-reactions.**

S-2 The second step in balancing by the "half-reaction" method is to balance all atoms, except hydrogen and oxygen, in each of the half-reactions Thus, for the half-reaction $Cl^- \rightarrow Cl_2$, the atoms are balanced to give $2Cl^- \rightarrow Cl_2$

Q-7 Balance all atoms except H and O in the following half-reaction

$$Cr_2O_7^{-2} \rightarrow Cr^{+3}$$

A-7 $Cr_2O_7^{-2} \rightarrow 2Cr^{+3}$

Q-8 Balance all atoms except H and O in the following half-reaction

$$Mn^{+2} \rightarrow MnO_4^- .$$

A-8 $Mn^{+2} \rightarrow MnO_4^-$

Q-9 Balance all atoms except H and O in the following half-reaction

$$Hg^{+2} \rightarrow Hg_2^{+2} .$$

A-9 $2Hg^{+2} \rightarrow Hg_2^{+2}$

R **The second step in balancing redox equations by the "half-reaction" method is to balance all atoms other than O and H in each half-reaction.**

S-3 The third step in balancing redox equations by the "half-reaction" method is to balance oxygen by adding water to the appropriate side of the equation and then adding H^+ ions to balance hydrogen. To balance the half-reaction $MnO_4^- \rightarrow Mn^{+2}$, add four H_2O to the right side of the equation. This gives $MnO_4^- \rightarrow Mn^{+2} + 4H_2O$. Then add eight H^+ ions to the left side of the equation to balance the hydrogen $8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$.

Q-10 Balance O and H in the following half-reaction

$$NO_2^- \rightarrow NO_3^-$$

A-10 $H_2O + NO_2^- \rightarrow NO_3^- + 2H^+$

Q-11 Balance O and H in the following half-reaction

$$Cr_2O_7^{-2} \rightarrow 2Cr^{+3}$$

A-11 $14H^+ + Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$

Q-12 Balance O and H in the following half-reactions

$$H_2S \rightarrow S$$

$$HNO_3 \rightarrow NO$$

A-12 $H_2S \rightarrow S + 2H^+$

$3H^+ + HNO_3 \rightarrow NO + 2H_2O$

Q-13 Balance O and H in the following half-reactions

$$HClO_3^- \rightarrow HClO_4$$

$$HClO_3 \rightarrow ClO_2$$

A-13 $HClO_3 + H_2O \rightarrow HClO_4 + 2H^+$

$H^+ + HClO_3 \rightarrow ClO_2 + H_2O$

R The third step in balancing by the "half-reaction" method is to balance oxygen by adding H_2O and then balance H by adding H^+.

S-4 The fourth step in balancing equations by the "half-reaction" method is to balance charges by adding electrons (e^-) as needed. The number and sign of charges on both sides of a balanced reaction must be the same. To balance the reaction

$$8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$$

five electrons must be added to the left side of the equation

$$5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$$

(total charge = +2) (total charge = +2)

If all four steps have been done correctly, one half-reaction will have electrons on the left hand side of the equation (the reduction half-reaction), while the other half-reaction will have electrons on the right hand side of the equation (the oxidation half-reaction)

Q-14 Balance charges in the two half-reactions

$$H_2O + NO_2^- \rightarrow NO_3^- + 2H^+$$

$$14H^+ + Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$$

A-14 $H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-$

(total charge = -1) (total charge = -1)

$6e^- + 14H^+ + Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$

(charge = +6) (charge = +6)

Q-15 Balance charges in the two half-reactions

$$S^{-2} \rightarrow S$$

$$4H^+ + NO_3^- \rightarrow NO + 2H_2O$$

A-15 $S^{-2} \rightarrow S + 2e^-$ (total charge on each side = -2)

$3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O$
(total charge on each side = 0)

Q-16 Balance charges in the two half-reactions

$$4H_2O + Mn^{+2} \rightarrow MnO_4^- + 8H^+$$

$$BiO_3^- + 6H^+ \rightarrow Bi^{+3} + 3H_2O$$

A-16 $4H_2O + Mn^{+2} \rightarrow MnO_4^- + 8H^+ + 5e^-$

$BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{+3} + 3H_2O$

Q-17 In the preceding answer, is Mn oxidized or reduced?

A-17 Mn is oxidized (loses electrons in the reaction shown)

Q-18 Balance charges in the half-reaction and indicate which is the oxidation and which is the reduction half-reaction

$$S^{-2} \rightarrow S$$

$$2H^+ + AsO_4^{-3} \rightarrow AsO_3^{-3} + H_2O$$

A-18 $S^{-2} \rightarrow S + 2e^-$ (oxidation)

$2e^- + 2H^+ + AsO_4^{-3} \rightarrow AsO_3^{-3} + H_2O$ (reduction)

R **In the fourth step of balancing redox equations by the "half-reaction" method, charges are balanced by adding electrons so that the total charge on both sides of the equation is equal. If the first four steps have been done correctly, one half-reaction will have electrons on the right hand side (oxidation) while the other equation will have the electrons on the left hand side of the equation (reduction).**

S-5 The fifth step in balancing by the "half-reaction" method is the addition of the two half-reactions in such a way that the electrons cancel out For the two half-reactions

$$Fe^{+2} \rightarrow Fe^{+3} + e^-$$

$$5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$$

the first reaction is multiplied by five and added to the second reaction to give

$$5Fe^{+2} + 8H^+ + MnO_4^- \rightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

Q-19 Show how the following half-reactions could be added so that electrons cancel and then add the equations.

$$H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-$$

$$6e^- + 14H^+ + Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$$

A-19 $3(H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-)$

$\underline{6e^- + 14H^+ + Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O}$

$3H_2O + 3NO_2^- + 14H^+ + Cr_2O_7^{-2} \rightarrow$

$3NO_3^- + 6H^+ + 2Cr^{+3} + 7H_2O$

Q-20 Show how the following half-reactions could be added so that electrons cancel and then add the equations.

$$S^{-2} \rightarrow S + 2e^-$$

$$3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O$$

(Hint: Both equations need to be multiplied by numbers.)

A-20 $3(S^{-2} \rightarrow S + 2e^-)$

$\underline{2(3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O)}$

$3S^{-2} + 8H^+ + 2NO_3^- \rightarrow 3S + 2NO + 4H_2O$

Q-21 Show how the following half-reactions could be added so that electrons cancel and then add the equations.

$$H_2O + ClO_3^- \rightarrow ClO_4^- + 2H^+ + 2e^-$$

$$2H^+ + e^- + ClO_3^- \rightarrow ClO_2 + H_2O$$

A-21 $H_2O + ClO_3^- \rightarrow ClO_4^- + 2H^+ + 2e^-$

$\underline{2(2H^+ + e^- + ClO_3^- \rightarrow ClO_2 + H_2O)}$

$H_2O + ClO_3^- + 4H^+ + 2ClO_3^- \rightarrow$

$2ClO_2 + 2H_2O + ClO_4^- + 2H^+$

Q-22 Show how the following half-reactions could be added so that electrons cancel and then add the equations

$4H_2O + Mn^{+2} \rightarrow MnO_4^- + 8H^+ + 5e^-$

$BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{+3} + 3H_2O$

A-22 $2(4H_2O + Mn^{+2} \rightarrow MnO_4^- + 8H^+ + 5e^-)$

$\underline{5(BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{+3} + 3H_2O)}$

$8H_2O + 2Mn^{+2} + 5BiO_3^- + 30H^+ \rightarrow$

$2MnO_4^- + 16H^+ + 5Bi^{+3} + 15H_2O$

R- **The fifth step in balancing is the addition of the two half-reactions in such a way that electrons cancel.**

S-6 The final step in balancing equations by the "half-reaction" method is to collect terms The balanced equation

$$H_2O + ClO_3^- + 4H^+ + 2ClO_3^- \rightarrow ClO_4^- + 2H^+ + 2ClO_2 + 2H_2O$$

has H_2O and H^+ indicated on each side of the equation Subtracting one H_2O and two H^+ from each side of the equation yields

$$ClO_3^- + 2H^+ + 2ClO_3^- \rightarrow ClO_4^- + 2ClO_2 + H_2O$$

If an oxidation-reduction reaction is carried out in a basic solution, then enough OH^- must be added to both sides of the balanced equation to neutralize all the H^+ (same number of OH^- added to each side). The balanced equation for the reaction between Fe^{+2} and MnO_4^- is

$$5Fe^{+2} + MnO_4^- + 8H^+ \rightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

If the reaction had been run in a basic solution, $8OH^-$ would be added to each side of the equation to yield

$$5Fe^{+2} + MnO_4^- + 8H_2O \rightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O + 8OH^-$$

To complete the balancing, $4H_2O$ should be subtracted from each side.

Q-23 Collect terms in the following balanced equation.

$3H_2S + 6H^+ + 2HNO_3 \rightarrow 3S + 6H^+ + 2NO$

$+ 4H_2O$

A-23 Subtract $6H^+$ from each side

$3H_2S + 2HNO_3 \rightarrow 3S + 2NO + 4H_2O$

Q-24 Collect terms in the following balanced equation.

$8H_2O + 2Mn^{+2} + 5BiO_3^- + 30H^+ \rightarrow$

$2MnO_4^- + 16H^+ + 5Bi^{+3} + 15H_2O$

A-24 Subtract $8H_2O$ and $16H^+$ from each side

$2Mn^{+2} + 5BiO_3^- + 14H^+ \rightarrow$

$2MnO_4^- + 5Bi^{+3} + 7H_2O$

Q-25 A reaction was conducted in a basic solution. The balanced equation by the half-reaction method was

$3N_2O_4 + Br^- + 3H_2O \rightarrow 6NO_2^- + BrO_3^- + 6H^+$

What is the correct balanced equation?

A-25 Add $6OH^-$ to each side and collect terms

$$3N_2O_4 + Br^- + 6OH^- \rightarrow 6NO_2^- + BrO_3^- + 3H_2O$$

Q-26 A reaction was conducted and gave a basic solution. The balanced equation by the "half-reaction" method was

$$2NO_3^- + 10K + 2H^+ \rightarrow N_2 + H_2O + 5K_2O$$

What is the correct balanced equation?

A-26 Add $2OH^-$ to each side and collect terms

$$2NO_3^- + 10K + H_2O \rightarrow N_2 + 2OH^- + 5K_2O$$

R. See S-7.

S-7 The steps in balancing redox equations by the "half-reaction" method are

a) Separate the equation into half-reactions

b) Balance all atoms except oxygen and hydrogen.

c) Balance oxygen by adding H_2O, balance hydrogen by adding H^+.

d) Balance charges by adding e^-

e) Add balanced half-reactions so e^- cancel.

f) Collect terms and neutralize H^+ with OH^- if necessary.

Q-27 Balance the following equation by the "half-reaction" method

$$S^{-2} + NO_3^- \rightarrow NO + S$$

(acidic solution)

A-27 Step 1 and 2

$S^{-2} \rightarrow S$

$NO_3^- \rightarrow NO$

Step 3

$S^{-2} \rightarrow S$

$4H^+ + NO_3^- \rightarrow NO + 2H_2O$

Step 4

$S^{-2} \rightarrow S + 2e^-$

$3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O$

Step 5 and 6

$3(S^{-2} \rightarrow S + 2e^-)$

$2(3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O)$

$3S^{-2} + 8H^+ + 2NO_3^- \rightarrow 3S + 2NO + 4H_2O$

Q-28 Balance the following equation by the "half-reaction" method

$$Cr^{+3} + Na_2O_2 \rightarrow CrO_4^- + Na^+$$

(basic solution)

A-28 Step 1 and 2

$Cr^{+3} \rightarrow CrO_4^-$

$Na_2O_2 \rightarrow 2Na^+$

Step 3

$4H_2O + Cr^{+3} \rightarrow CrO_4^- + 8H^+$

$4H^+ + Na_2O_2 \rightarrow 2Na^+ + 2H_2O$

Step 4

$4H_2O + Cr^{+3} \rightarrow CrO_4^- + 8H^+ + 4e^-$

$2e^- + 4H^+ + Na_2O_2 \rightarrow 2Na^+ + 2H_2O$

Step 5 and 6

$1(4H_2O + Cr^{+3} \rightarrow CrO_4^- + 8H^+ + 4e^-)$

$2(2e^- + 4H^+ + Na_2O_2 \rightarrow 2Na^+ + 2H_2O)$

$$4H_2O + Cr^{+3} + 8H^+ + 2Na_2O_2 \rightarrow CrO_4^- + 8H^+ + 4Na^+ + 4H_2O$$

Collect terms

$Cr^{+3} + 2Na_2O_2 \rightarrow CrO_4^- + 4Na^+$

Q-29 Balance the following equation by the "half-reaction" method

$Zn + NO_3^- \rightarrow Zn^{+2} + NO_2$

(acidic solution)

A-29 $1(Zn \rightarrow Zn^{+2} + 2e^-)$

$2(NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O)$

$Zn + 2NO_3^- + 4H^+ \rightarrow Zn^{+2} + 2NO_2 + 2H_2O$

Q-30 Balance the following equation by the "half-reaction" method

$MnO_4^- + H_2O_2 \rightarrow MnO_2 + O_2$

(basic solution)

A-30 $2(MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O)$

$3(H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-)$

$$2MnO_4^- + 8H^+ + 3H_2O_2 \rightarrow 2MnO_2 + 4H_2O + 3O_2 + 6H^+$$

Collect terms

$$2H^+ + 2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 4H_2O + 3O_2$$

add OH^- to both sides and collect terms

$$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 2H_2O + 3O_2 + 2OH^-$$

Q-31 Balance the following equation by the "half-reaction" method

$NO_2^- + Cr_2O_7^{-2} \rightarrow NO_3^- + Cr^{+3}$

(acidic solution)

A-31 $3(H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-)$

$1(Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O)$

$$3H_2O + 3NO_2^- + Cr_2O_7^{-2} + 14H^+ \rightarrow 3NO_3^- + 2Cr^{+3} + 7H_2O + 6H^+$$

Collect terms

$3NO_2^- + Cr_2O_7^{-2} + 8H^+ \rightarrow 3NO_3^- + 2Cr^{+3} + 4H_2O$

Q-32 Balance the following equation by the "half-reaction" method.

$CrO_2^- + IO_3^- \rightarrow I^- + CrO_4^{-2}$

(basic solution)

A-32 $2(CrO_2^- + 2H_2O \rightarrow CrO_4^{-2} + 4H^+ + 3e^-)$

$\underline{1(6e^- + IO_3^- + 6H^+ \rightarrow I^- + 3H_2O)}$

$2CrO_2^- + 4H_2O + IO_3^- + 6H^+ \rightarrow 2CrO_4^{-2} + 8H^+ + I^- + 3H_2O$.

add OH^-, collect terms

$2CrO_2^- + 2OH^- + IO_3^- \rightarrow 2CrO_4^{-2} + I^- + H_2O$

Balance the following equations by the "half-reaction" method
The final equation obtained in each case should be checked to see if it is balanced.

$Cr_2O_7^{-2} + I_2 \rightarrow Cr^{+3} + IO_3^-$ (acidic solution)

$PbO_2 + Cl^- \rightarrow ClO^- + Pb(OH)_3^-$ (basic solution)

$MnO_4^{-2} \rightarrow MnO_2 + MnO_4^-$ (acidic solution)

$HO_2^- + Cr(OH)_3^- \rightarrow CrO_4^{-2} + OH^-$ (basic solution)

$SbH_3 + Hg_2^{+2} \rightarrow Sb + Hg$ (acidic solution)

$MnO_4^- + N_2H_4 \rightarrow Mn^{+2} + NH_2OH$ (acidic solution)

$Al + NO_3^- \rightarrow Al(OH)_4^- + NH_3$ (basic solution)

$I_2 + H_2S \rightarrow I^- + S$ (acidic solution)

Table I

STANDARD OXIDATION-REDUCTION POTENTIALS, ACID SOLUTIONS

(After Latimer)

Potential (Volts)	Half Reaction
3 02	$Li \rightleftharpoons Li^+ + e^-$
2 92	$K \rightleftharpoons K^+ + e^-$
2 90	$Ba \rightleftharpoons Ba^{2+} + 2e^-$
2 87	$Ca \rightleftharpoons Ca^{2+} + 2e^-$
2 71	$Na \rightleftharpoons Na^+ + e^-$
2 34	$Mg \rightleftharpoons Mg^{2+} + 2e^-$
1.67	$Al \rightleftharpoons Al^{3+} + 3e^-$
1 05	$Mn \rightleftharpoons Mn^{2+} + 2e^-$
0 828	$H_2 + 2OH^- \rightleftharpoons 2H_2O + 2e^-$
0 762	$Zn \rightleftharpoons Zn^{2+} + 2e^-$
0 71	$Cr \rightleftharpoons Cr^{3+} + 3e^-$
0 440	$Fe \rightleftharpoons Fe^{2+} + 2e^-$
0 41	$Cr^{2+} \rightleftharpoons Cr^{3+} + e^-$
0 402	$Cd \rightleftharpoons Cd^{2+} + 2e^-$
0 355	$Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-$
0 250	$Ni \rightleftharpoons Ni^{2+} + 2e^-$
0 136	$Sn \rightleftharpoons Sn^{2+} + 2e^-$
0 126	$Pb \rightleftharpoons Pb^{2+} + 2e^-$
0.000	$H_2 \rightleftharpoons 2H^+ + 2e^-$
-0.141	$H_2S \rightleftharpoons S + 2H^+ + 2e^-$
-0 15	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$
-0 167	$Cu^+ \rightleftharpoons Cu^{2+} + e^-$
-0 345	$Cu \rightleftharpoons Cu^{2+} + 2e^-$
-0.45	$S + 3H_2O \rightleftharpoons H_2SO_3 + 4H^+ + 4e^-$
-0.522	$Cu \rightleftharpoons Cu^+ + e^-$
-0.535	$2I^- \rightleftharpoons I_2 + 2e^-$
-0.682	$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^-$
-0.771	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$
-0.7986	$2Hg \rightleftharpoons Hg_2^{2+} + 2e^-$
-0.7995	$Ag \rightleftharpoons Ag^+ + e^-$
-0.854	$Hg \rightleftharpoons Hg^{2+} + 2e^-$
-0.91	$Hg_2^{2+} \rightleftharpoons 2Hg^{2+} + 2e^-$
-0.94	$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$
-1 065	$2Br^- \rightleftharpoons Br_{2(\ell)} + 2e^-$
-1.229	$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$
-1.358	$2Cl^- \rightleftharpoons Cl_2 + 2e^-$
-1.36	$2Cr^{3+} + 7H_2O \rightleftharpoons Cr_2O_7^{2-} + 14H^+ + 6e^-$
-1.42	$Au \rightleftharpoons Au^{3+} + 3e^-$
-1 44	$Br^- + 3H_2O \rightleftharpoons BrO_3^- + 6H^+ + 6e^-$
-1.45	$Cl^- + 3H_2O \rightleftharpoons ClO_3^- + 6H^+ + 6e^-$
-1.456	$Pb^{2+} + 2H_2O \rightleftharpoons PbO_2 + 4H^+ + 2e^-$
-1.52	$Mn^{2+} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5e^-$
-1.67	$MnO_2 + 2H_2O \rightleftharpoons MnO_4^- + 4H^+ + 3e^-$
-1.685	$PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$
-2.01	$2SO_4^{2-} \rightleftharpoons S_2O_8^{2-} + 2e^-$
-2.07	$O_2 + H_2O \rightleftharpoons O_3 + 2H^+ + 2e^-$
-2.85	$2F^- \rightleftharpoons F_2 + 2e^-$

NOTES

Chapter 10 ACIDS, BASES, AND COMPLEX IONS

Part I Acids and Bases

After completing this section you should

a) understand the limitations of the Arrhenius and Bronsted-Lowry definitions
b) be able to recognize the conjugate acid-base pairs in a reaction
c) be able to give the relative acid and base strengths of reactants and products from the equilibrium position of a reaction
d) understand the Lewis definition and be able to determine the Lewis acid and base in a reaction
e) be able to predict relative acid-base strength on the basis of the predicted stability of ions

Part II Amphoteric Properties

After completing this section you should

a) know the eleven elements which form amphoteric hydroxides and the group of elements which form acidic and basic hydroxides or oxides
b) be able to devise schemes for the analysis and separation of certain metal ions in solution

Part III· Metallic Complex Ions

After completing this section you should

a) be able to recognize the metallic ion and the ligand in a complex ion
b) be able to predict from magnetic moment and X-ray structure determinations which orbitals of the metallic ion are involved in bonding with the ligand of a complex ion
c) know the elements which readily form complex ions, and how complex ion formation can be used for the analysis and separation of metallic ions in solution

PART I: Acids and Bases

S-1 Through the years, several important theories about acids and bases have evolved The Arrhenius, Bronsted-Lowry, and Lewis theories will be considered

Svante Arrhenius proposed in 1887 that an acid was an aqueous solution with more H^+ than OH^- ions and a base was an aqueous solution with more OH^- than H^+ ions According to Arrhenius, HCl and NaOH formed acidic and basic solutions, respectively, because of the dissociation described by the following equations

$$HCl \rightleftarrows H^+ + Cl^-$$
$$NaOH \rightleftarrows OH^- + Na^+$$

Q-1 Acetic acid (CH_3COOH) is dissolved in water Would Arrhenius have considered the resulting solution acidic? Why?

(Hint: Acetic acid dissociates in water according to the reaction
$CH_3COOH \rightleftarrows CH_3COO^- + H^+$)

A-1 Yes The solution is aqueous and contains an excess of H^+ ions because of the equilibrium

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

Q-2 Would an aqueous solution of H_2S be considered acidic according to the Arrhenius theory? Why?

A-2 Yes The solution is aqueous and contains an excess of H^+ ions because of the equilibrium

$$H_2S \rightleftarrows H^+ + HS^- \rightleftarrows S^{-2} + 2H^+$$

Q-3 Would gaseous HCl be considered an Arrhenius acid? Why?

A-3 No Arrhenius defined acids as aqueous solutions containing excess H^+. His theory is not applicable to non-aqueous solutions, gases or solids.

Q-4 Would pure acetic acid, a liquid with a boiling point of 118°, be considered an acid in the Arrhenius sense?

A-4 No Pure acetic acid is not an aqueous solution, therefore, it cannot be considered an Arrhenius acid.

Q-5 A solution of 0 56 g $Ca(OH)_2$ in 1000 ml of water was prepared. Would the solution be considered basic by the Arrhenius definition? Why?

A-5 Yes The aqueous solution would contain an excess of OH^- because of the reaction

$$Ca(OH)_2 \rightleftarrows Ca^{+2} + 2OH^-$$

Q-6 Gaseous NH_3 dissolves in water to form NH_4OH. Would a water solution of ammonia (NH_3) be considered an Arrhenius base? Why?

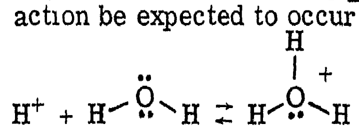
A-6 Yes, because the aqueous solution contains excess OH^- ions

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Q-7 Ammonia gas also dissolves in diethyl ether ($CH_3CH_2OCH_2CH_3$) Would an ether solution of ammonia be considered basic in the Arrhenius sense? Why?

A-7 No, because the Arrhenius definition is applicable only to aqueous solutions Diethyl ether is a non-aqueous liquid

Q-8 The proton (H^+) is much smaller than a H atom and has a very high charge density Would the following hydration reaction be expected to occur? Why?



A-8 Yes In water, the oxygen atom has a partial negative charge and has two pair of unshared electrons The proton would be strongly attracted to the oxygen in water

Q-9 The equilibrium constant for the reaction given in Q-8 is very large Would H^+ or H_3O^+ be present in higher concentration in an aqueous solution of HCl? How do you know?

A-9 H_3O^+ is present in higher concentration For all practical purposes H^+ does not exist in aqueous solution. The large equilibrium constant indicates that the $[H_3O^+]/[H^+]$ ratio is very large

Q-10 If the hydrated proton is represented as H_3O^+ (referred to as hydronium ion), write the chemical reaction which occurs when gaseous HBr is dissolved in water

A-10 $HBr_{(g)} + H_2O \rightleftharpoons H_3O^+ + Br^-$

Q-11 Write the chemical reaction which occurs when acetic acid (CH_3COOH) is dissolved in water

A-11 $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

Q-12 When ammonia dissolves in water, hydroxyl ions (OH^-) and ammonium ions (NH_4^+) are formed

Write the chemical equation which indicates the reaction between ammonia and water

A-12 $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Q-13 In the reaction of ammonia with water, does the water gain or lose a proton?

A-13 Water loses a proton, and ammonia gains a proton

Q-14 In the reaction of gaseous HBr with water (A-10), does the water gain or lose a proton?

A-14 Water gains a proton and HBr loses a proton.

S-2 In 1923 the Danish chemist Bronsted and the English chemist Lowry independently defined acids and bases in more general terms The Bronsted-Lowry theory defines an acid as a proton donor and a base as a proton acceptor

Q-15 In the reaction

$HCl_{(g)} + H_2O \rightleftharpoons H_3O^+ + Cl^-$

HCl functions as a Bronsted-Lowry acid Why?

A-15 HCl donates a proton to water

Q-16 In the reaction of gaseous HCl with water, what is the solvent (water) considered in the Bronsted-Lowry sense?

A-16 Since water accepts a proton, it is considered a base in the Bronsted-Lowry sense

Q-17 In the reaction

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$,

which reactant, NH_3 or H_2O, is considered the Bronsted-Lowry base? Acid? Why?

A-17 NH_3 accepts a proton from water Therefore, NH_3 is a base and H_2O is an acid

Q-18 When HBr gas is bubbled through triethylamine, $(CH_3CH_2)_3N$:, the following reaction occurs

$(CH_3CH_2)_3N: + HBr \rightleftharpoons (CH_3CH_2)_3NH^+ + Br^-$

Which reactant would be considered a Bronsted-Lowry acid? Base? Why?

A-18 In the reaction, HBr donates a proton HBr is the acid Triethylamine accepts a proton $(CH_3CH_2)_3N$ is the base

Q-19 For the reaction given in Q-18, what would be the Arrhenius acid?

A-19 Since the reaction occurs in a non-aqueous system, the Arrhenius definition of acids is not applicable.

B According to the Bronsted-Lowry definition, an acid is a proton donor and a base is a proton acceptor.

S-3 When an acid loses a proton, a basic ion is formed Thus, when the acid HBr ionizes,

$$HBr \rightleftharpoons H^+ + Br^-$$

the basic ion Br^- is formed When the basic ion Br^- accepts a proton, the acid HBr is formed The acid HBr and ion Br^- are said to be a conjugate acid-base pair The Br^- ion, which can accept a proton to form an acid, is called the conjugate base, while the acid formed is called the conjugate acid

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Q-20 The ionization of nitric acid is represented as

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

HNO_3 is said to be a conjugate acid and NO_3^- is said to be a conjugate base In terms of loss or gain of a proton, how are <u>conjugate</u> acids and <u>conjugate</u> bases related?

A-20 A conjugate acid forms a conjugate base by the loss of a proton A conjugate base forms a conjugate acid by accepting a proton

Q-21 In the reaction of a proton with water,

$$H^+ + H_2O \rightleftharpoons H_3O^+,$$

water is considered the conjugate base What must be considered the conjugate acid?

A-21 H_3O^+ must be considered the conjugate acid When H_3O^+ loses a proton, it forms H_2O, the conjugate base

Q-22 Perchloric acid dissociates in water according to the reaction

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$$

In this reaction, $HClO_4$ functions as a Bronsted-Lowry acid What is the conjugate base of $HClO_4$?

A-22 The conjugate base of $HClO_4$ is ClO_4^-

Q-23 For the reaction given in Q-22, what is the relationship between H_2O and H_3O^+?

A-23 H_2O is a conjugate base (proton acceptor) and H_3O^+ is a conjugate acid.

Q-24 For the reaction of phosphoric acid with water,

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-,$$

give the conjugate acid-base pairs

A-24 H_3PO_4 is the conjugate acid of the conjugate base $H_2PO_4^-$ H_2O is the conjugate base of the conjugate acid H_3O^+

Q-25 For the reaction of triethylamine, $(CH_3CH_2)_3N$, with HBr (see Q-18), what are the conjugate acid-base pairs?

A-25 HBr is the conjugate acid and Br^- is the conjugate base. Triethylamine is the conjugate base and $(CH_3CH_2)_3NH^+$ is the conjugate acid

[redacted]

S-4 In a reaction involving the transfer of a proton, the weaker acid and the weaker base will tend to form In the reaction of a strong acid HA with the strong base B^-,

$$HA + B^- \rightleftharpoons HB + A^-$$

the weaker acid HB and the weaker base A^- will be formed

Q-26 The reaction of acetic acid with OH^- ion goes nearly to completion

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

What is the relative acid strength of water and acetic acid?

A-26 Water is a weaker acid than acetic acid

Q-27 What is the relative base strength of CH_3COO^- (acetate ion) and OH^-?

A-27 Acetate ion is a weaker base than OH^-

Q-28 The reaction of ammonium ion (NH_4^+) with water shifts far to the left

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

What is the relative base strength of ammonia and water?

A-28 Because reactions tend to form the weakest acid and base, ammonia must be a stronger base than water

Q-29 The reaction

$$HClO_4 + HSO_4^- \rightleftharpoons H_2SO_4 + ClO_4^-$$

shifts far to the right.

Which is the stronger acid, H_2SO_4 or $HClO_4$? How do you know?

A-29 Reactions tend to give the weakest acids, therefore, H_2SO_4 must be a weaker acid than $HClO_4$

Q-30 The reaction

$$CH_3\overset{\overset{O}{\|}}{C}OH + HSO_4^- \rightleftharpoons H_2SO_4 + CH_3\overset{\overset{O}{\|}}{C}O^-$$

shifts far to the left. Which is the stronger acid, H_2SO_4 or acetic acid?

A-30 Sulfuric acid is a stronger acid than acetic acid

Q-31 The reaction

$$H_2SO_4 + Cl^- \rightleftharpoons HCl + HSO_4^-$$

shifts far to the right. Which is the stronger acid, HCl or H_2SO_4?

A-31 H_2SO_4 is a stronger acid than HCl.

Q-32 When HCl is added to a solution of bicarbonate ion (HCO_3^-), CO_2 is formed because of the decomposition of H_2CO_3

$$HCl + HCO_3^- \rightarrow H_2CO_3 + Cl^-$$

$$H_2CO_3 \rightarrow CO_2 + H_2O.$$

Which is the stronger acid, HCl or H_2CO_3?

A-32 HCl is the stronger acid Because H_2CO_3 is formed, the reaction

$$HCO_3^- + HCl \rightleftarrows H_2CO_3 + Cl^-$$

must shift far to the right, indicating H_2CO_3 is the weaker acid

Q-33 When acetic acid is added to a solution of bicarbonate ions, CO_2 is formed Which acid is the stronger, CH_3COOH or H_2CO_3?

A-33 Acetic acid is the stronger acid

Q-34 When phenol (C_6H_5OH) is added to a solution of NaOH, the reaction

$$C_6H_5OH + OH^- \rightleftarrows C_6H_5O^- + H_2O$$

shifts far to the right Which is the stronger acid, water or phenol?

A-34 Phenol is a stronger acid

Q-35 When phenol is added to a solution of bicarbonate ion, little CO_2 is formed Which acid is the stronger, H_2CO_3 or C_6H_5OH?

A-35 H_2CO_3 is the stronger acid The reaction

$$HCO_3^- + C_6H_5OH \rightleftarrows H_2CO_3 + C_6H_5O^-$$

shifts far to the left

R **Proton transfer reactions tend to form the weakest acids and the weakest bases The comparative strength of acids discussed in this section is**

Strongest	**$HClO_4$**	**ClO_4^-**	**Weakest Base**
	H_2SO_4	**HSO_4^-**	
	HCl	**Cl^-**	
	CH_3COOH	**CH_3COO^-**	
	H_2CO_3	**HCO_3^-**	
Weakest Acid	**C_6H_5OH**	**$C_6H_5O^-$**	**Strongest**

S-5 Water is a weak acid but forms a very strong conjugate base (OH^-) Perchloric acid ($HClO_4$) is a very strong acid, but forms a very weak conjugate base (ClO_4^-) Strong acids form weak conjugate bases and weak acids form strong conjugate bases

Q-36 In comparison to water, NH_3 is a very weak acid Compare the strength of the bases OH^- and NH_2^-

A-36 The base NH_2^- is stronger than OH^- Weak acids form strong conjugate bases.

Q-37 Ammonia is a much stronger acid than methane (CH_4) or ethane (C_2H_6) Compare the strength of the bases NH_2^- and CH_3^-

A-37 The CH_3^- ion must be a stronger base than the amide ion (NH_2^-)

Q-38 Amide ion (NH_2^-) is added to water What will the reaction be? Indicate the predominate direction for the equilibrium.

A-38 $NH_2^- + H_2O \rightleftarrows OH^- + NH_3$

OH^- is a weaker base than NH_2^-

NH_3 is a weaker acid than H_2O

Q-39 If CH_3^- ion is added to liquid ammonia, what is the reaction? Indicate the predominate direction for the equilibrium

A-39 $CH_3^- + NH_3 \rightleftarrows CH_4 + NH_2^-$

R Weak acids yield strong conjugate bases. Strong acids yield weak conjugate bases.

S-6 Lewis, an American chemist, proposed a much more general definition for acids and bases Acids are <u>electron pair acceptors</u> and bases are <u>electron pair donors</u> In the reaction of a proton with water, the proton accepts a pair of electrons from the oxygen of water (acts as an acid) and the water donates a pair of electrons to the proton (acts as a base)

Q-40 In the reaction

$NH_3 + H^+ \rightarrow NH_4^+$

does NH_3 act like a Lewis acid or base? Why?

A-40 Base It is an electron pair donor

Q-41 In the reaction

$Ag^+ + Cl^- \rightarrow AgCl,$

would chloride ion be considered a Lewis base? Why?

A-41 Chloride ion is a Lewis base in this reaction It donates electrons to silver

Q-42 In the reaction

$SnCl_4 + 2Cl^- \rightarrow SnCl_6^{-2}$

would $SnCl_4$ be considered a Lewis base? Why?

A-42 No $SnCl_4$ acts as an electron acceptor, a Lewis acid

Q-43 In the reaction

$$(CH_3)_3N + B(CH_3)_3 \rightarrow (CH_3)_3N\text{-}B(CH_3)_3$$

which molecule acts as the Lewis base?

A-43 $(CH_3)_3N$ donates electrons to $B(CH_3)_3$

Q 44 $B(CH_3)_3$ is an electron acceptor, a Lewis acid How many electrons does the boron atom have in its outside shell in trimethyl boron, $B(CH_3)_3$?

A-44 six

$$\begin{array}{l} CH_3 \\ \times \\ B \times CH_3 \\ \times \\ CH_3 \end{array}$$

Q-45 How many electrons does aluminum have in its outermost shell in the compound $AlCl_3$?

A-45 six

Cl
x
Al x Cl
x
Cl

Q-46 Both $(CH_3)_3B$ and $AlCl_3$ can act as Lewis acids Why can the central atom in these substances accept a pair of electrons?

A-46 The central atoms (B, Al) have only six electrons in their outside shell By accepting an electron pair, the octet is completed.

Q-47 In the following compound, which atom would you expect to act as electron acceptor? Why?

Cl ^{x} Be ^{x} Cl

A-47 Be, because it has only four electrons in its outermost shell Gaining two electron pairs would complete the octet

Q-48 For the following compound, which atom would you expect to function as as electron acceptor? Why?

H
x
H^{x} C $\overset{x}{\circ}$ Mg $_{\circ}$ Br
x
H

methylmagnesium bromide

A-48 Mg, because it has only four electrons in its outermost shell Gaining two electron pairs would complete the octet

Q-49 Dimethylether acts as a Lewis base Which atom functions as the electron donor? Why?

H H
x x
H x C ^{x} O ^{x} C x H
x x
H H

A-49 Oxygen, because it has two pairs of unshared electrons which it can share with or donate to a Lewis acid.

Q-50 Will the following compound function as a Lewis acid or base? Which atom(s) is responsible for the property?

H
x
H x C ^{x} Cl
x
H

methyl chloride

A-50 Lewis base. Cl acts as the electron donor because it has three pairs of unshared electrons to donate to a Lewis acid.

Q-51 Each of the following compounds can function as a Lewis base Why?

CH_3OH methyl alcohol

CH_3NH_2 methylamine

CH_3F methyl flouride

A-51 Each compound contains an atom with unshared pairs of electrons These electrons can be shared with a Lewis acid.

$CH_3\ddot{O}H$, $CH_3\ddot{N}H_2$, $CH_3\ddot{F}:$

Q-52 Which of the three compounds mentioned in Q-51 would be the <u>best</u> electron donor? Why?

(Hint What are the electronegativities of the basic atoms?)

A-52 The best donor is CH_3NH_2 and the poorest is CH_3F. The electronegativity of F is greater than O which is greater than N. F holds its electrons very tightly

Q-53 Which of the following compounds would you expect to be the best Lewis base? Why?

$CH_3CH_2OCH_2CH_3$

diethyl ether

$CH_3CH_2N(H)CH_2CH_3$

diethylamine

A-53 Diethylamine. Nitrogen has a lower electronegativity than oxygen

Q-54 Which of the following species would you expect to be most basic in the Lewis sense? Why?

OH^- or F^-

A-54 OH^- is a much better electron donor than F^-

Q-55 Arrange the following Lewis bases in order of increasing electron donor ability

CH_3^-, NH_2^-, OH^-, F^-

A-55 most basic (best donor) CH_3^-

NH_2^-

OH^-

least basic F^-

Q-56 In view of the answer to Q-55, what would the order of acid strength be for the acids

CH_4, NH_3, H_2O, HF

A-56 most acidic HF

H_2O

NH_3

least acidic CH_4

R Lewis acids are electron acceptors and Lewis bases are electron donors. A strong acid yields a weak conjugate base while a strong base yields a weak conjugate acid.

S-7 The base strength of negative ions will be inversely proportional to the stability of the ion. The F^- ion is more stable than the CH_3^- ion and F^- is a weaker base than CH_3^-. For the series CH_3^-, NH_2^-, OH^-, F^-, the relative base strengths and, consequently, the relative stabilities of ions can be predicted from the electronegativity of the central atom. As electronegativity increases, the stability of the ion increases. Another factor affecting stability of ions is the distribution of charge in the ion. Distribution of charge in a large volume tends to stabilize the ion. Thus, all other things being equal, large ions are more stable than small ions.

Q-57 Consider the ions, F^-, Cl^-, Br^-, I^-. On the basis of electronegativity alone, which ion is most stable? Which ion is the best electron donor?

A-57 F^- is most stable, based on electronegativity alone F has the highest electronegativity I^- would be the best electron donor because it has the smallest electronegativity of the four halides	Q-58 Based upon electronegativity alone, which acid would be the strongest, HF, HCl, HBr, or HI?
A-58 HF On the basis of electronegativity, F^- is the weakest base, therefore, HF would be the strongest acid	Q-59 Based upon size alone, which ion would be the most stable, F^-, Cl^-, Br^-, or I^-? Which ion would be the best electron donor?
A-59 I^- would be the most stable, based upon size alone, because I^- is the largest ion of the series Based on size alone, F^- would be the least stable and the best electron donor	Q-60 Based upon size alone, which would be a stronger acid, HF or HCl?
A-60 HCl On basis of size alone, F^- is a stronger base (electron donor) than Cl^-, therefore, HF would be a weaker acid than HCl	Q-61 K_{diss} for HF is 6 9 x 10^{-4} while K_{diss} for HBr is very large Which ion, F^- or Br^-, is a better electron donor?
A-61 F^- HF is a weaker acid, therefore, F^- is a stronger base	Q-62 Which ion, Br^- or F^- is more stable?
A-62 Br^- F^- is more basic and less stable.	Q-63 What is, apparently, the more important factor governing the stability of the halide ions, electronegativity or size?
A-63 Size. On the basis of size Br^- is more stable than F^- On the basis of electronegativity F^- is more stable.	Q-64 Which of the following ions would you expect to be more stable? Why? OH^- HS^-
A-64 OH^- on the basis of electronegativity HS^- on the basis of ion size	Q-65 Which of the following is a stronger acid, H_2O or H_2S?
A-65 H_2S is a stronger acid	Q-66 Which of the ions is more basic, OH^- or HS^-? What is the more important factor governing the stability of the ion?
A-66 OH^-. If H_2S is a stronger acid, HS^- must be a weaker base. Size is the more important factor governing stability of the ion.	Q-67 In proceeding down a group of a periodic table, size tends to be a more important factor governing acidity of binary acids. Within periods, electronegativity tends to be a more important factor governing acidity of binary acids. Which of the following ions is more stable? HS^- or HTe^-

A-67 HTe^- This ion is larger than HS^-

Q-68 Which ion would be expected to be more basic?

NH_2^- or AsH_2^-

A-68 NH_2^- would be more basic, and AsH_2^- the more stable ion

Q-69 Which of the following would be expected to be the stronger acid?

H_3P or H_3Sb

A-69 H_3Sb H_2Sb^- would be the more stable ion, and the weaker base, therefore, H_3Sb would be the stronger acid

R Increasing electronegativity tends to stabilize negative ions; increasing size tends to stabilize ions.

S-8 As the oxidation state of an atom increases, the electronegativity of the atom increases. The electronegativity of an atom is also changed by attaching other groups to the atom Thus, chlorine in $HClO_4$ is more electronegative than in $HClO_3$ because of the difference in oxidation state The nitrogen in NH_2Cl is more electronegative than in NH_3 because of the influence of the strong electron withdrawing properties of chlorine. As the electronegativity of the central atom of a negative ion increases, the stability of the ion increases Thus, ClO_4^- is a more stable ion than ClO_3^- and $NHCl^-$ is more stable than NH_2^-

Q-70 H-O-Cl is a stronger acid than H-O-Br Offer an explanation.

A-70 OCl^- is a more stable ion than OBr^- Chlorine is more electronegative than bromine, thus, the oxygen in OCl^- is more electronegative than in OBr^- The size of the ion must not be the determining factor

Q-71 Which ion would be expected to be a stronger base?

```
   H          H
   |          |
Cl-C⁻   or  H-C⁻
   |          |
   H          H
```

Why?

(Hint. the more stable the ion, the weaker the base)

A-71

```
  H
  |
H-C⁻
  |
  H
```

is a stronger base $ClCH_2^-$ is more stable because the electronegativity of carbon is increased by chlorine.

Q-72 Which ion would be expected to be more stable? Why?

$Cl\text{-}O^-$ or $O\text{-}Cl\text{-}O^-$

A-72 $O\text{-}Cl\text{-}O^-$ is more stable because the chlorine has a higher oxidation number than in ClO^-.

Q-73 Which is a stronger acid? Why?

```
    O            O
    |            |
HO-Cl-O  or  H-O-Cl-O
                 |
                 O
```

A-73

```
      O
      |
H-O-Cl-O
      |
      O
```

The ClO_4^- ion is more stable than the ClO_3^- ion because chlorine has a higher oxidation state in ClO_4^-

Q-74 Methyl (CH_3-) is <u>less</u> electronegative than hydrogen ($H-$). Which of the following ions is more stable? Why?

CH_3O^- or HO^-

A-74 OH^- is more stable. The CH_3 group <u>decreases</u> the electronegativity of the oxygen, thus decreasing the stability of CH_3O^-

Q-75 Which of the following would be expected to function as a better Lewis base? Why?

CH_3OCH_3 or CH_3OH

A-75 CH_3OCH_3. Both CH_3 groups would tend to <u>decrease</u> the electronegativity of the oxygen

Q-76 While methyl (CH_3-) has an electronegativity less than hydrogen, $CH_3C(=O)-$ has an electronegativity much greater than hydrogen

Offer an explanation as to why compound A is more acidic than compound B

$CH_3C(=O)-OH$ (A) CH_3CH_2OH (B)

A-76 The ion $CH_3C(=O)-O^-$ would be more stable than $CH_3CH_2O^-$ because the acyl group ($CH_3C(=O)-$) increases the electronegativity of oxygen

Q-77 <u>One</u> of the following compounds is considered basic. Which one is the base? Why isn't the other compound a base?

$CH_3CH_2N(H)-H$ (ethylamine) $CH_3C(=O)-NH_2$ (acetamide)

A-77 Ethylamine is the base. Acetamide is not a base because the acyl group increases the electronegativity of the nitrogen so much that the nitrogen is not a good electron donor

R **Stability of ions is a function of electronegativity and charge distribution in the ion. The electronegativity of an atom increases as the oxidation state increases. The electronegativity of an atom may also be increased by bonding the atom to a more highly electronegative group or atom.**

S-9 Arrhenius acids and bases are restricted to aqueous solutions of H^+ and OH^- ions. Bronsted-Lowry acids and bases are more general and include all proton donors and proton acceptors. The Lewis definition of acids and bases is still more general: acids are electron acceptors - bases are electron donors.

Q-78 Indicate the Lewis acid and base in the following reaction.

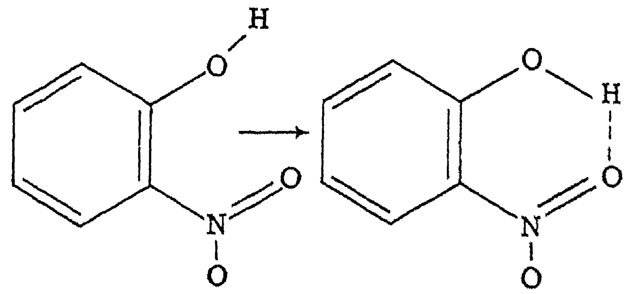
$AlCl_3 + Cl_2 \rightarrow AlCl_4^-Cl^+$

A-78 The Lewis acid is

Cl
x
Al x Cl
x
Cl

The Lewis base is Cl x Cl

Q-79 Indicate the Lewis acid and the Lewis base in the following reaction



o-nitrophenol

A-79 The electron acceptor is H of the –OH group The electron donor is O of the $-NO_2$ group

Q-80 Is *o*-nitrophenol a Lewis acid or a Lewis base?

A-80 Both In the reaction shown in Q-79, both the acidic and basic groups were in the same molecule

Q-81 In the following reaction does CH_3OH (methyl alcohol) function as a Lewis acid or a Lewis base?

$$CH_3OH + NH_2^- \rightleftharpoons CH_3O^- + NH_3$$

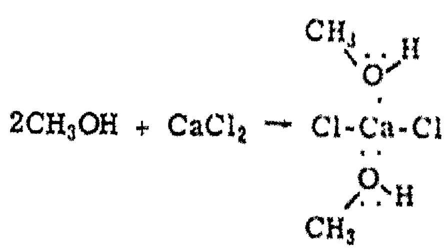
A-81 Lewis acid The OH hydrogen in methyl alcohol accepts the electrons which are donated by the NH_2^- group (Lewis base)

Q-82 In the following reaction, does methyl alcohol function as an acid or a base?

$$CH_3OH + H^+ \rightleftharpoons \left[CH_3O\begin{matrix} H \\ H \end{matrix}\right]^+$$

A-82 A Lewis base The O in methyl alcohol is an electron donor

Q-83 In the following reaction, does methanol (methyl alcohol) function as a Lewis acid or base?



A-83 As a Lewis base. $CaCl_2$ acts as a Lewis acid (electron acceptor).

Q-84 Is methanol (methyl alcohol) an acid or a base?

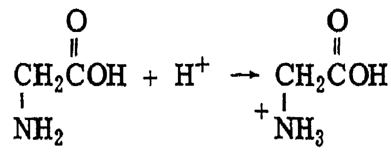
A-84 Both In Q-81, CH_3OH acted as an acid, in Q-82 and 83, CH_3OH acted as a base

Q-85 In the following reaction does glycine (an amino acid) function as an acid or a base?

$$\underset{NH_2}{\underset{|}{CH_2}}\overset{O}{\overset{\|}{C}}OH + OH^- \rightarrow H_2O + \underset{NH_2}{\underset{|}{CH_2}}\overset{O}{\overset{\|}{C}}O^-$$

A-85 As an acid (a proton donor)

Q-86 In the following reaction does glycine function as an acid or a base?



A-86 As a base (a proton acceptor or an electron donor)

R Some compounds can function as both acids and bases.

PART II: Amphoteric Properties

S-1 Certain compounds can function either as acids (proton donors or electron acceptors) or as bases (proton acceptors or electron pair donors) Such compounds are said to be <u>amphoteric</u>

Q-1 A certain metal hydroxide, MOH, known to be amphoteric, was added to a basic solution (one containing an excess of OH^- ions).

Write an equation showing how MOH could act like a <u>proton donor</u> in this solution

A-1 $MOH + OH^- \rightleftharpoons MO^- + H_2O$

Q-2 The amphoteric metal hydroxide MOH, was added to an acidic solution Write an equation showing how MOH could act like a <u>proton acceptor</u> in this solution.

A-2 $MOH + H^+ \rightleftharpoons MOH_2^+$, or

$MOH + H^+ \rightleftharpoons M^+ + H_2O$

Q-3 Write and balance the reaction of MOH (acting as a base) reacting with the acid HCl

A-3 $MOH + HCl \rightleftharpoons Cl^- + H_2O + M^+$ or

$MOH + HCl \rightleftharpoons Cl^- + MOH_2^+$

Q-4 Write and balance the reaction of MOH (acting as an acid) reacting with the base KOH

A-4 $MOH + KOH \rightleftharpoons H_2O + K^+ + MO^-$

Q-5 Write and balance the reaction of MOH (acting as an acid) reacting with the base H_2O.

A-5 $MOH + H_2O \rightleftarrows H_3O^+ + MO^-$

Q-6 The oxides of elements display varying degrees of amphoterism Some oxides act equally well as acids or bases; others are better acids than bases and vice versa Some elements form hydroxides and oxides which act only as acids or as bases Solid NaOH is added to water. Does the NaOH function as an acidic, basic or amphoteric hydroxide?

A-6 A strong base
$NaOH \rightleftarrows Na^+ + OH^-$

Q-7 Solid LiOH is added to water Does LiOH function as an acidic or a basic hydroxide?

A-7 A strong base
$LiOH \rightleftarrows Li^+ + OH^-$

Q-8 When added to water, do the hydroxides of all the Group I elements, Li, Na, K, Rb, Cs, and Fr, function as acidic, basic, or amphoteric hydroxides?

A-8 Strong bases

Q-9 In water solution, the compound HOCl has acidic properties but not basic properties. Would the hydroxide of iodine (HOI) be expected to exhibit acidic, basic, or amphoteric properties in an aqueous solution?

A-9 Acidic properties

Q-10 In water solutions do the hydroxides of the Group VII elements function as acidic, basic, or amphoteric hydroxides?

A-10 Acidic hydroxides

[redacted]

S-2 The following table shows the eleven elements which form amphoteric oxides or hydroxides The elements to the right of the amphoteric elements in each period (except Cr^{+6}) form acidic oxides In the fourth period, the elements to the right of Ge form acidic oxides. Except for H and Be, all elements in groups I_A, II_A, and III_B form basic oxides.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA
H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr^{+3}	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At

	Q-11 Do any periods lack amphoteric elements?
A-11 No. All periods have at least one amphoteric element.	Q-12 What are the amphoteric elements in the first three periods?
A-12 H, Be, Al	Q-13 Write the formula of the amphoteric hydroxides of each of the amphoteric elements in the first three periods.
A-13 HOH, $Be(OH)_2$, $Al(OH)_3$	Q-14 In moving from H to Li and from Be to Mg, how do the acidic, basic, or amphoteric properties of the elements change?
A-14 Change from amphoteric to basic.	Q-15 The properties of the elements change from acidic to amphoteric to basic in moving down the periodic chart B is acidic What kind of properties should Al be expected to have?
A-15 Amphoteric or basic properties, Aluminum is amphoteric.	Q-16 Ge is amphoteric What kind of properties should Si be expected to have?
A-16 Either amphoteric or acidic properties. Silicon forms an acidic oxide.	Q-17 Mg has basic properties What kind of properties should Ca be expected to have?
A-17 Basic properties.	Q-18 PbO_2 (element 82) is an amphoteric oxide What properties would be expected for Bi_2O_5 (element 83)?
A-18 Amphoteric or acidic properties. Bi_2O_5 is an acidic oxide	Q-19 P_2O_5 (element 15) is an acidic oxide. What properties would be expected for SiO_2 (element 14)?
A-19 Acidic or amphoteric. SiO_2 is an acidic oxide.	Q-20 If $B(OH)_3$ is acidic and $Al(OH)_3$ (Al is directly beneath B) is amphoteric, will $Ga(OH)_3$ (Ga is directly beneath Al) be an acidic, basic, or amphoteric hydroxide?
A-20 Amphoteric or basic. $Ga(OH)_3$ is, in fact, amphoteric.	Q-21 If $Cd(OH)_2$ is a basic oxide, will HgO (Hg is directly beneath Cd) be an acidic, basic, or amphoteric oxide?
A-21 Basic oxide.	

S-3 Keeping the generalizations in mind that the trends from acidic, to amphoteric, to basic properties occur in moving <u>down</u> the chart (for example H_3BO_3 and $Al(OH)_3$) a second generalization can be made

In most cases, if an element forms an amphoteric hydroxide in the M^{+n} oxidation state, the hydroxides of a higher oxidation state (e g , n + 1) will be more acidic and those in a lower oxidation state (e. g , n - 1) will be more basic For example, Cr_2O_3, is an amphoteric oxide while CrO_3 is an acidic oxide Keep in mind, however, that the distinction between amphoteric, acidic, and basic properties is quite arbitrary

	Q-22 Which of the following is amphoteric ? $Cr(OH)_3$ or CrO_3
A-22 $Cr(OH)_3$ is amphoteric	Q-23 If $Cr(OH)_3$ is amphoteric, would CrO_3 be an acidic, basic, or amphoteric oxide ?
A-23 Acidic oxide	Q-24 If Sb_2O_3 is an amphoteric oxide, would Sb_2O_5 be a basic oxide ? Why ?
A-24 No The oxidation state of antimony in Sb_2O_5 is +5, while in Sb_2O_3 the oxidation state is +3. As the oxidation state increases, the oxides become more acidic. Sb_2O_5 is an <u>acidic</u> oxide	Q-25 SnO_2 is an amphoteric oxide. Would SnO be a more acidic or a more basic oxide than SnO_2 ?
A-25 Because the oxidation state of Sn in SnO is lower than in SnO_2, SnO should be a more basic oxide. Both SnO and SnO_2 are considered amphoteric oxides, however	Q-26 Which one of the following is amphoteric P_2O_5, OsO_4, In_2O_3
A-26 In_2O_3	Q-27 Which one of the following is amphoteric ? PbO, Bi_2O_5, As_2O_5
A-27 PbO	Q-28 Which one of the following is amphoteric ? NiO, CoO, ZnO
A-28 ZnO	Q-29 Which one of the following is amphoteric ? CaO, $Sn(OH)_2$, $Fe(OH)_3$
A-29 $Sn(OH)_2$	Q-30 Which one of the following is amphoteric ? NiO, PbO_2, Bi_2O_5
A-30 PbO_2	Q-31 Which one of the following is amphoteric ? P_2O_5, As_2O_5, Sb_2O_3

A-31 Sb_2O_3	Q-32 Which one of the following is amphoteric BeO, MgO, Se_2O_3
A-32 BeO	Q-33 Which one of the following is amphoteric Ag_2O, Au_2O, Cu_2O
A-33 None of these are amphoteric	Q-34 Which one of the following is amphoteric' Fe_2O_3, Co_2O_3, NiO
A-34 None of these are amphoteric	Q-35 Which one of the following is not amphoteric? CO_2, GeO_2, PbO_2
A-35 CO_2	Q-36 Which one of the following is not amphoteric? ZnO, In_2O_3, CdO
A-36 CdO	Q-37 Which one of the following is not amphoteric? $Ga(OH)_3$, SnO_2, Bi_2O_5
A-37 Bi_2O_5	

S-4 The acidic, basic and amphoteric properties of elements serve as the basis of a method for the separation and analysis of mixtures containing various metal ions Basic oxides and hydroxides are more soluble in acidic solutions than in water while acidic oxides and hydroxides are more soluble in basic solutions than in water Amphoteric oxides and hydroxides, however, are more soluble in either acidic and basic solutions than in water

	Q-38 A solution was known to contain only one of two ions, Sn(IV) or As(V) Dropwise addition of 6M NaOH to this solution produced a precipitate which dissolved when excess NaOH was added Which ion was present?
A-38 As(V) will not precipitate in a basic solution (As_2O_5 is an acidic oxide) On the other hand, Sn(IV) is amphoteric and will form a precipitate of $Sn(OH)_4$ in a weakly basic solution The $Sn(OH)_4$ will dissolve in excess base. Therefore, the precipitate must have been SnO_2 ($Sn(OH)_4$) which, upon addition of more base, formed SnO_3^{-2} $Sn(IV) + 6OH^- \rightleftarrows Sn(OH)_4 + 2OH^- \rightleftarrows SnO_3^{-2} + 3H_2O$ $As(V) + 8OH^- \rightleftarrows AsO_4^{-3} + 4H_2O$	Q-39 A solution was known to contain only one of two ions, Ni^{+2} or Zn^{+2} When 6M NaOH was added to this solution a precipitate formed The precipitate did not dissolve in excess NaOH What ion was indicated?

A-39 Both ions would form precipitates, namely $Ni(OH)_2$ and $Zn(OH)_2$ Of these two compounds, only $Zn(OH)_2$ is amphoteric $Zn(OH)_2$ should dissolve (forming ZnO_2^{-2}) in excess NaOH Because the precipitate did not dissolve in NaOH, Ni^{+2} is indicated in the original solution

$$Ni^{+2} + 3OH^- \rightleftharpoons \underset{\text{no reaction}}{\underset{\downarrow}{Ni(OH)_2 + OH^-}}$$

$$Zn^{+2} + 4OH^- \rightleftharpoons Zn(OH)_2 + 2OH^- \rightleftharpoons ZnO_2^{-2} + 2H_2O$$

The ion must be Ni^{+2}

Q-40 A solution contained only one of two ions, Cr(III) or As(V) Addition of one drop of 6M NaOH produced no precipitate Continued addition of 6M NaOH did not produce a precipitate What conclusions can be drawn?

A-40 Cr(III) would be expected to produce a precipitate which, being amphoteric, would dissolve in excess base

$$Cr^{+3} + 4OH^- \rightleftharpoons Cr(OH)_3 + OH^- \rightleftharpoons CrO_2^- + 2H_2O$$

As(V) does not form a precipitate in a basic solution

Q-41 $Fe(OH)_3$ will dissolve only slightly in strong base How could one separate $Fe(OH)_3$ from $Al(OH)_3$?

A-41 Add 3M NaOH to the mixture. The $Fe(OH)_3$ will remain as a solid, the $Al(OH)_3$ will dissolve.

Q-42 Suggest a method for separating a mixture of ZnO and HgO

A-42 Add 3M NaOH. The ZnO is an amphoteric oxide and will dissolve in NaOH. HgO is not amphoteric and will not dissolve.

$$Zn(OH)_2 + 2OH^- \rightleftharpoons ZnO_2^{-2} + 2H_2O$$

Q-43 A solution was known to contain only one of the following ions: Fe(III), Zn(II), Al(III) or Pb(II).

A drop of 6M NaOH was added. A precipitate formed. What could be concluded?

A-43 Nothing All of the ions would give the reaction described.

Q-44 The precipitate formed in Q-43 did not dissolve in 1 ml of 3M NaOH What could be concluded?

A-44 The precipitate was $Fe(OH)_3$. All the other hydroxides (oxides) are amphoteric.

Q-45 A solution was known to contain two of the following ions: Hg(II), As(V), Al(III), and Zn(II). A drop of 6M NaOH added to the solution caused a precipitate, which redissolved when excess NaOH was added. What conclusion can be made about the composition of the solution?

A-45 Hg(II) would have formed the basic oxide, HgO, which would not have redissolved Therefore, Hg(II) was not present Since As(V) would not have precipitated under these conditions, it might have been present Both Al(III) and Zn(II) would have precipitated and redissolved as described Therefore, it must be concluded that Hg(II) was not present, but two of the other three were present Further tests would be necessary in order to determine which two ions were present

Q-46 A solution was known to contain one of the following ions.

Pb(II), Ag(I) or Cu(II).

When a drop of 6M NaOH was added to the solution, a precipitate formed. The precipitate dissolved in excess 6M NaOH What conclusions can be reached regarding the composition of the solution?

A-46 Of the three ions, only Pb(II) is amphoteric. Therefore, the ion present must be Pb(II) Had Ag(I) or Cu(II) been present, a precipitate would have formed that was insoluble in excess NaOH

Q-47 A strongly basic solution contained Sn(IV) ions How could $Sn(OH)_4$ be obtained from this solution?

A-47 HCl could be carefully added until a precipitate formed Addition of HCl would reduce the OH^- concentration shifting the following equilibrium to the left

$$Sn(OH)_4 + 2OH^- \rightleftharpoons SnO_3^{-2} + 3H_2O$$

If too much acid is added $Sn(OH)_4$ will dissolve

$$Sn(OH)_4 + 4H^+ \rightleftharpoons 4H_2O + Sn(IV)$$

Q-48 It has been observed that when a solution containing Al(III) ions is treated with NH_4OH, a precipitate forms which <u>does not</u> redissolve in excess NaOH Explain

(Hint the precipitate formed using NH_4OH is $Al(OH)_3$
K_b for $NH_4OH = 1\ 8 \times 10^{-5}$.)

A-48 In order for $Al(OH)_3$ to dissolve in base, a fairly large concentration of OH^- ions is needed to shift the equilibrium to the right.

$$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2H_2O$$

NaOH provides a sufficiently large concentration of OH^-, but NH_4OH does not because it is such a weak base ($K_b = 1.8 \times 10^{-5}$).

Q-49 Solid $Pb(OH)_2$ will dissolve in excess NaOH but will not dissolve in concentrated NH_4OH Explain.

A-49 Since $Pb(OH)_2$ is amphoteric, it will dissolve in a solution containing a high concentration of OH^- (e.g a NaOH solution). The OH^- concentration in NH_4OH solution is too low (because NH_4OH is a weak base) to cause the $Pb(OH)_2$ to dissolve.

$$Pb(OH)_2 + 2OH^- \rightleftharpoons PbO_2^{-2} + 2H_2O$$

Q-50 Solid $Ca(OH)_2$ is insoluble in both concentrated NH_4OH and NaOH solutions. Explain

A-50 $Ca(OH)_2$ is a basic hydroxide which is insoluble in basic solutions.

Q-51 A solid mixture consists of $Pb(OH)_2$ and $Ca(OH)_2$. Describe a method of separating these two compounds.

A-51 $Pb(OH)_2$ is amphoteric and will dissolve in an excess of NaOH solution leaving solid $Ca(OH)_2$.

$$Pb(OH)_2 + 2OH^- \rightleftarrows PbO_2^{-2} + 2H_2O$$

The $Pb(OH)_2$ can be recovered from the NaOH solution by carefully adding HCl until the solution is neutral.

Q-52 For a solution containing one of the following two ions, which reagent, NaOH, NH_4OH, or HCl, would be useful in determining which ion is present? Which ion precipitates? Which ion remains in solution?

Al(III) or Fe(III) in an acidic solution.

A-52 Excess NaOH. AlO_2^- would remain in solution while $Fe(OH)_3$ would precipitate.

Q-53 For a solution containing one of the following two ions, which reagent, NaOH, NH_4OH, HCl, would be useful in determining which ion is present? Which ion precipitates? Which ion remains in solution?

Fe(III), Sn(IV) in acidic solution.

A-53 Excess NaOH. SnO_3^{-2} will remain in solution while $Fe(OH)_3$ will precipitate.

R Amphoteric properties are useful in separating and identifying various ionic species.

PART III: Metallic Complex Ions

S-1 Metallic complex ions or compounds are formed when a metallic ion combines with an ion or molecule which is an electron pair donor. An example of a complex ion is $[Co(NH_3)_6]^{+3}$. The metallic cation (Co^{+3}) is called the <u>central ion</u>, and the ion or molecule (in this case, NH_3) which combines with it is called the <u>ligand.</u>

Q-1 In the complex ion, $[Cu(NH_3)_4]^{+2}$, what is the central ion and what is the ligand?

A-1 central ion Cu^{+2}
ligand NH_3

Q-2 What is the central ion and what is the ligand in the complex ion $[Fe(CN)_6]^{-3}$?

A-2 central ion Fe^{+3}
ligand CN^-

Q-3 What is the central ion and what is the ligand in the complex ion $[Co(H_2O)_5Cl]^{+2}$?

A-3 central ion Co^{+3}
ligands H_2O, Cl^-

Q-4 What is the charge on the central ion in the complex ion $[Co(NH_3)_5Cl]^{+2}$?

A-4 chloride ion is -1
NH_3 is neutral (0)
cobalt (Co) is +3

Q-5 What is the charge on the central ion in $[Fe(H_2O)Cl_4]^-$?

A-5 chloride ion is -1
H_2O is neutral (0)
iron (Fe) is +3

Q-6 What orbitals are being filled in transition metals?

A-6 The d-orbitals are being filled.

Q-7 The electronic structure of the Fe atom, a $3d^6\ 4s^2$ configuration, can be represented as follows.

3d: ↑↓ ↑ ↑ ↑ ↑ 4s: ↑↓ 4p: _ _ _

Write the electronic structure for the Fe^{+3} ion.

(Hint In the formation of the ion the 4s electrons are lost before the 3d electrons

---

A-7 Fe^{+3}

3d: ↑ ↑ ↑ ↑ ↑ 4s: _ 4p: _ _ _

Q-8 If the zinc atom is $3d^{10}\ 4s^2$, write the electronic structure for Zn^{+2}

A-8 Zn^{+2}

3d: ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ 4s: _ 4p: _ _ _

Q-9 If the nickel atom is $3d^8\ 4s^2$, write the electronic structure for Ni^{+2}.

A-9 Ni^{+2}

3d: ↑↓ ↑↓ ↑↓ ↑ ↑ 4s: _ 4p: _ _ _

Q-10 If the chromium atom has a $3d^4\ 4s^2$ configuration, write the electronic structure for Cr^{+3}

A-10 Cr^{+3}

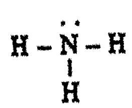
3d: ↑ ↑ ↑ _ _ 4s: _ 4p: _ _ _

Q-11 Why would all the ions in the preceding examples be able to act as Lewis acids (electron acceptors)?

A-11 All the ions have unfilled orbitals in their valence shells and thus have the capacity to accept electrons.

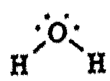
Q-12 A common ligand in complex ions is NH_3. Write the Lewis structure for NH_3 (a neutral ligand)

A-12



Q-13 Write the Lewis structure for water (a neutral ligand).

A-13



Q-14 Write the Lewis structure for the CN^- ion (a charged ligand).

A-14 $\overset{-}{.C \equiv N^{\cdot}}$

Q-15 What do all these structures have in common with regard to unshared electrons?

A-15 All the ligands have at least one unshared pair of electrons

Q-16 Are ligands Lewis acids or Lewis bases?

A-16 All ligands are Lewis bases (electron donors).

R Complex ions consist of a central ion (Lewis acid) and ligands (Lewis base).

S-2 Since all the central cations have unfilled orbitals and the ligands have unshared electron pairs, it seems reasonable that a bond between the central ion and the ligand will be a coordinate covalent bond in which both the electrons are from the ligand. In order to determine which orbitals of the central ion are involved in the bonding, experimental data are needed. Magnetic moment and X-ray structure determinations give the necessary data.

An electron spinning on its own axis produces a magnetic field. If a substance has unpaired electrons, magnetism results and it is said to be paramagnetic. If all the electrons in a substance are paired, the magnetic fields produced by the spinning electrons cancel each other and the substance is said to be diamagnetic.

Q-17 The magnetic moment, μ, is related to the number of unpaired electrons, n, by the following equation.

μ (Bohr Magnetons) $= \sqrt{n(n+2)}$

If n = 1, calculate μ.

A-17 $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3}$
$= 1.7$ B. M.

Q-18 If n = 2, calculate the value of μ.

A-18
$$\mu = \sqrt{n(n+2)}$$
$$= \sqrt{2(2+2)}$$
$$= \sqrt{8} \quad = 2.8 \text{ B. M.}$$

Q-19 If $\mu = 3.9$, calculate n, the number of unpaired electrons.

(Hint. The quadratic formula is $\dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$.)

A-19
$$\mu = \sqrt{n(n+2)}$$
$$3.9 = \sqrt{n(n+2)}$$

Squaring both sides of the equation yields

$$15 = n(n+2)$$
$$15 = n^2 + 2n$$
$$n^2 + 2n - 15 = 0$$
$$n = \frac{-2 \pm \sqrt{(2)^2 - 4(1)(-15)}}{2}$$
$$n = \frac{-2 \pm \sqrt{64}}{2} = \frac{-2 \pm 8}{2} = +3 \text{ or } -5$$

Since n must be a positive number, n = 3 (n could also be obtained by factoring the equation, $n^2 + 2n - 15 = 0$)

Q-20 If n = 4, calculate μ.

A-20 $\mu = \sqrt{n(n+2)}$
$= \sqrt{4(4+2)} = \sqrt{24}$
$= 4.9$ B M

Q-21 If $\mu = 5.9$, calculate n.

A-21 $\mu = \sqrt{n(n+2)}$
$5.9 = \sqrt{n(n+2)}$

Squaring both sides of the equation yields

$35 = n(n+2)$

$n^2 + 2n = 35$

$n^2 + 2n - 35 = 0$

Application of the quadratic formula gives

$$n = \frac{-2 \pm \sqrt{(2)^2 - 4(1)(-35)}}{2}$$

$$= \frac{-2 \pm 12}{2}$$

n = 5 = number of unpaired electrons

[redacted]

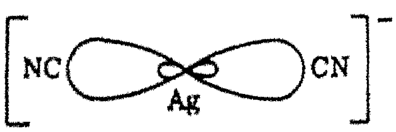
S-3 X-ray examination is useful because it gives the geometrical configuration of the complex ion. Since specific types of hybridization are associated with specific geometrical configurations, a knowledge of the geometry of the molecule and of the number of unpaired electrons indicates which orbitals of the cation are involved in the bonding.

Q-22 What is the angle between the lobes of sp hybrid orbitals?

A-22 180°

Q-23 If $[Ag(CN)_2]^-$ is a linear ion, what type of hybridization would you suggest for the cation of this molecule? Sketch the complex ion showing the hybridized orbitals.

A-23 sp hybridization.



Q-24 If the cyanide ion has a -1 charge, what is the charge on the silver ion in the $[Ag(CN)_2]^-$ complex ion?

A-24 Ag is +1.

Q-25 If the Ag atom is $4d^{10}\ 5s^1$, what is the electron structure of Ag^+?

A-25 Ag^+

4d					5s	5p		
↑↓	↑↓	↑↓	↑↓	↑↓	__	__	__	__

Q-26 The magnetic moment of $[Ag(CN)_2]^-$ is equal to zero. How many unpaired electrons does the Ag^+ ion have in this complex?

A-26 If $\mu = 0$, $n = 0$
(no unpaired electrons)

Q-27 If ligands are Lewis bases (i.e., electron donors) and the central ions have empty valence orbitals, how will the bond between the ligand and the central ion be formed?

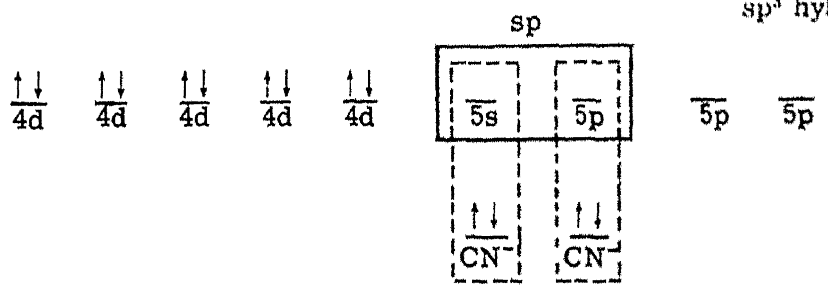
A-27 The bond is formed by donation of the unshared pair of electrons on the ligand to the metal ion.

Q-28 What is the name given to the bond between two atoms in which both of the electrons in the bond came originally from one of the atoms?

A-28 Coordinate covalent bond.

Q-29 If $[Ag(CN)_2]^-$ is a sp hybrid, suggest an electronic structure for the complex ion (show ligands donating electrons to the empty orbitals on the cation).

A-29 $[Ag(CN)_2]^-$

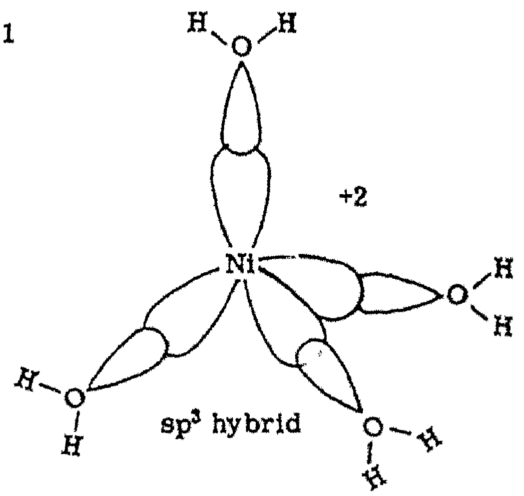


Q-30 What are the angles between the lobes of sp^3 hybrid orbitals?

A-30 109° (tetrahedron)

Q-31 If the $[Ni(H_2O)_4]^{+2}$ ion has a tetrahedral configuration, what hybridization would be predicted for this ion? Sketch the complex ion.

A-31



Q-32 What is the charge on the nickel ion in the $[Ni(H_2O)_4]^{+2}$ complex?

A-32 Water is neutral.
Ni is +2.

Q-33 If the nickel atom is $3d^8\,4s^2$, what is the electronic structure of Ni^{+2}?

A-33 Ni^{+2}

3d					4s	4p		
↑↓	↑↓	↑↓	↑	↑	__	__	__	__

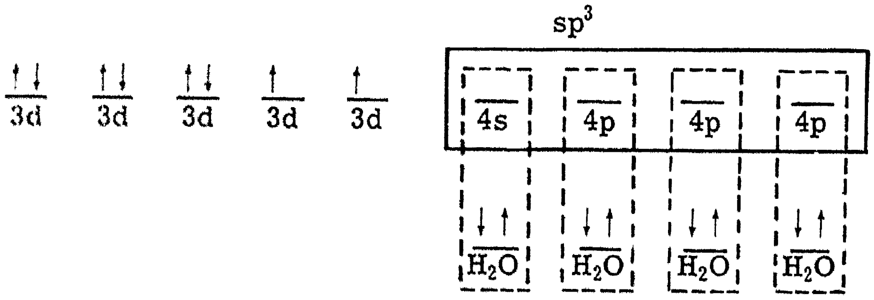
Q-34 The magnetic moment of the $[Ni(H_2O)_4]^{+2}$ complex is 2.8 B. M. How many unpaired electrons does the complex have?

A-34 If μ = 2.8 B.M., then n = 2

(Refer to A-18 for calculations.)

Q-35 If the Ni ion is an sp^3 hybrid, suggest an electronic structure for $[Ni(H_2O)_4]^{+2}$ based on a magnetic moment of 2.8 B.M.

A-35 $[Ni(H_2O)_4]^{+2}$



Q-36 What are the angles between the lobes of dsp^2 hybrid orbitals?

A-36 90° (square planar)

Q-37 If the $[Cu(H_2O)_4]^{+2}$ complex is square planar, what hybridization would be predicted for this ion?

A-37 dsp^2

Q-38 What is the charge on Cu in $[Cu(H_2O)_4]^{+2}$?

A-38 H_2O is neutral.

Cu is +2.

Q-39 If the Cu atom is $3d^9\ 4s^2$, what is the electronic structure of Cu^{+2}?

A-39 Cu^{+2}

3d 4s 4p

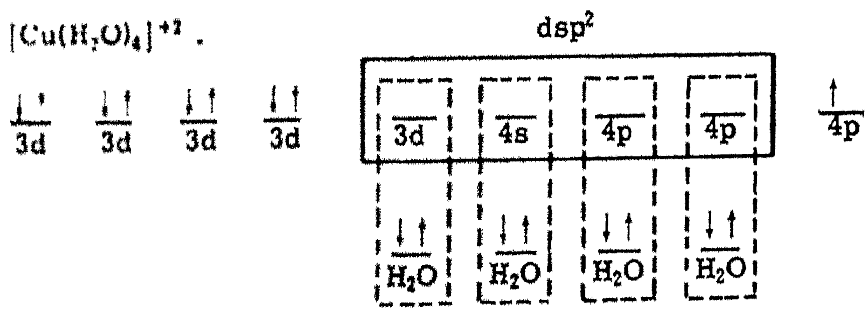
↑↓ ↑↓ ↑↓ ↑↓ ↑ __ __ __ __

Q-40 The magnetic moment of $[Cu(H_2O)_4]^{+2}$ is 1.8 B.M. How many unpaired electrons does the complex ion have?

A-40 If μ = 1.8, n = 1 (one unpaired electron)

Q-41 Predict an electronic structure for the $[Cu(H_2O)_4]^{+2}$ complex ion if it has a value of μ equal to 1.8 B.M. and a square planar configuration.

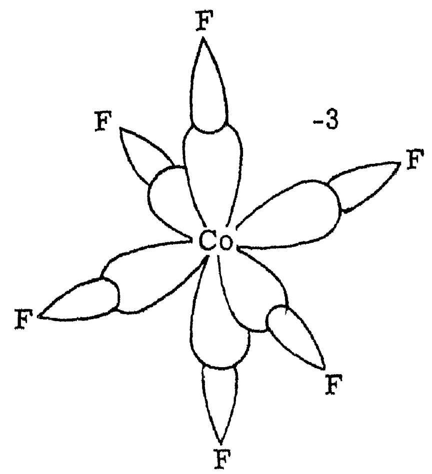
A-41 $[Cu(H_2O)_4]^{+2}$.



Note that this configuration calls for promotion of an electron from a 3d to a 4p orbital.

Q-42 The $[CoF_6]^{-3}$ ion has an octahedral configuration. The two types of hybridization associated with an octahedral configuration are d^2sp^3 or sp^3d^2. Sketch the $[CoF_6]^{-3}$ ion showing the hybrid orbitals.

A-42



Q-43 What is the charge on the Co ion in the complex ion $[CoF_6]^{-3}$?

A-43 Fluoride is -1.
Co is +3.

Q-44 If the cobalt atom is $3d^7 4s$, write the electronic structure of Co^+

A-44 Co^{+3}

3d 4s 4p

↑↓ ↑ ↑ ↑ ↑ __ __ __ __

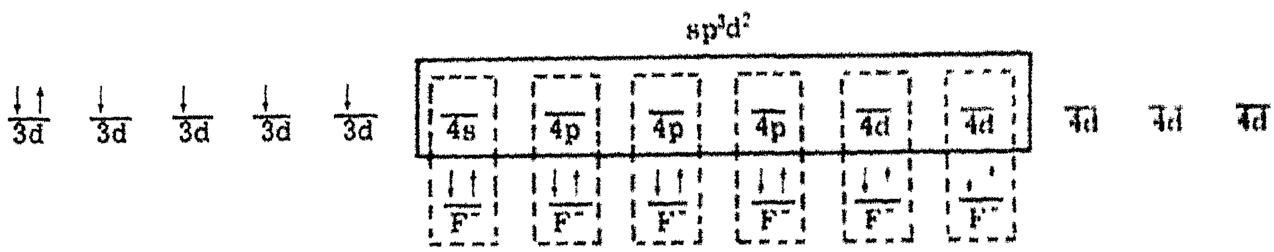
Q-45 The magnetic moment of $[CoF_6]^{-3}$ is 5.3 B M How many unpaired electrons does it have?

A-45 If μ = 5.3, n = 4 (four unpaired electrons)

Q-46 Predict an electronic structure for the $[CoF_6]^{-3}$ ion if its magnetic moment is 5.3 B. M. and it is an octahedral ion

A-46 $[CoF_6]^{-3}$

Q-47 If the $[Co(CN)_6]^{-3}$ ion is octahedral, what hybridization would be predicted for it?



A-47 d^2sp^3 or sp^3d^2 hybrids.

Q-48 What is the charge on the Co ion in the $[Co(CN)_6]^{-3}$ complex?

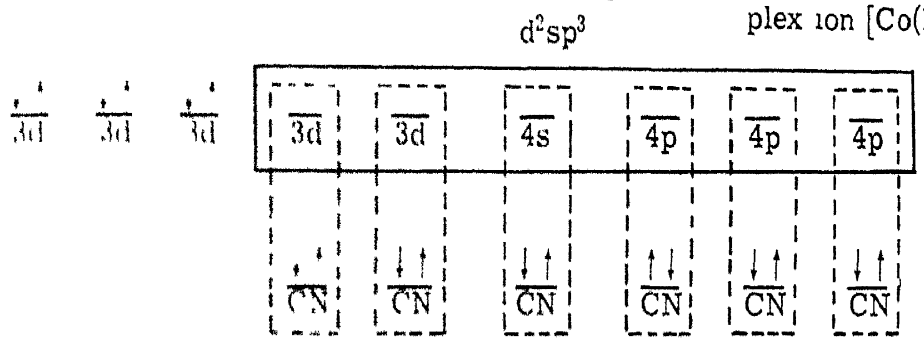
A-48 Since cyanide has a -1 charge, cobalt must have a +3 charge.

Q-49 The magnetic moment of $[Co(CN)_6]^{-3}$ is 0.0. How many unpaired electrons does the complex have?

A-49 If μ = 0, n = 0 (no unpaired electrons)

Q-50 Write an electronic structure for $[Co(CN)_6]^{-3}$ based on the experimental data (octahedral configuration and ... 0)

A-50 $[Co(CN)_6]^{-3}$



Q-51 What is the charge on cobalt in the complex ion $[Co(NH_3)_6]^{+3}$?

A-51 NH_3 is neutral, therefore Co is +3

Q-52 If the complex ion $[Co(NH_3)_6]^{+3}$ is octahedral, what hybridization would be predicted?

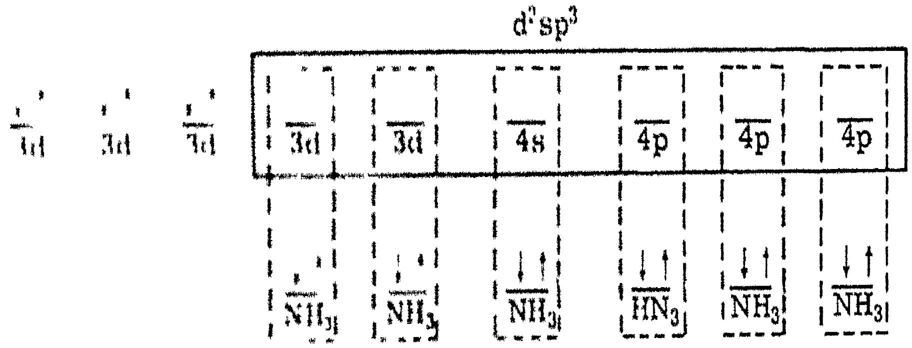
A-52 d^2sp^3 or sp^3d^2 hybrids.

Q-53 Given that the magnetic moment of $[Co(NH_3)_6]^{+3}$ equals 0.0, write an electronic structure for the complex based on this value.

A-53 d^2sp^3 hybrid

μ, n = 0 (no unpaired electrons)

$[Co(NH_3)_6]^{+3}$

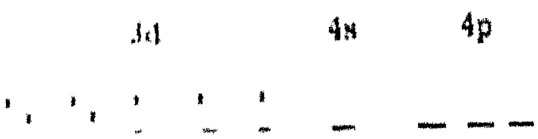


Q-54 What is the charge on cobalt in the complex ion $[Co(NO_2)_6]^{-4}$ if the NO_2 ligand is -1?

A-54 NO_2 is -1, therefore Co is +2.

Q-55 What is the electronic structure for Co^{+2}?

A-55 Co^{+2}



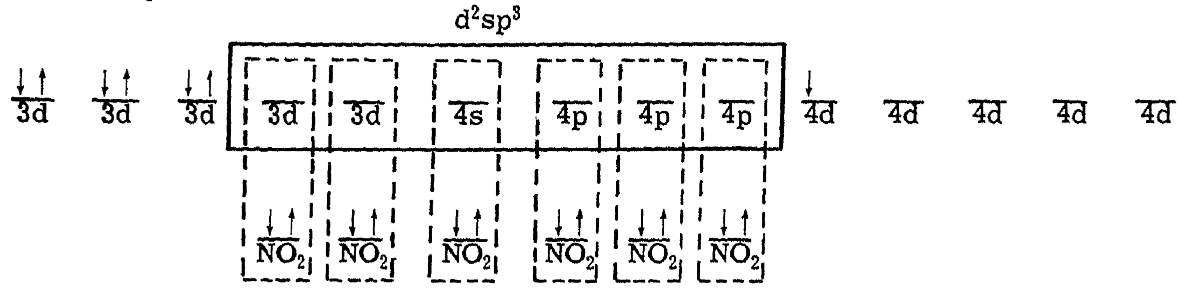
Q-56 If the $[Co(NO_2)_6]^{-4}$ complex is octahedral, what hybridization would be predicted for this ion?

A-56 d^2sp^3 or sp^3d^2 hybrids.

Q-57 The magnetic moment, μ, for $[Co(NO_2)_6]^{-4}$ is 1.9 B M. Predict an electronic structure for the complex based on this value.

A-57 d^2sp^3 $\mu = 1.9$, $n = 1$

$[Co(NO_2)_6]^{-4}$



Q-58 What is the charge on the silver ion in $[Ag(NH_3)_2]^{+}$?

A-58 Since NH_3 is neutral, Ag must be +1

Q-59 What is the electronic structure of Ag^{+}?

A-59 Ag^{+} is $4d^{10}$

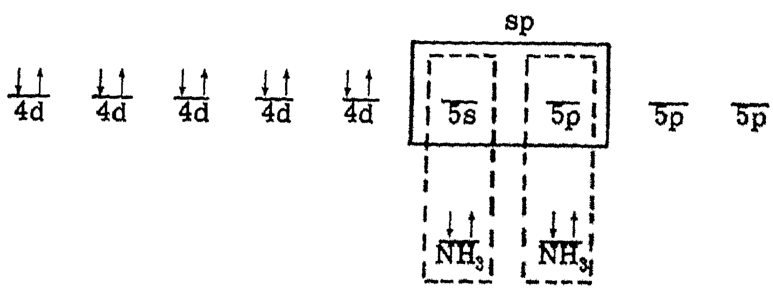
4d 5s 5p

↑↑ ↑↓ ↑↓ ↑↓ ↑↓ __ __ __ __

Q-60 If the $[Ag(NH_3)_2]^{+}$ ion is linear, propose an electronic structure for the complex ion.

A-60 sp hybridization

$[Ag(NH_3)_2]^{+}$



Q-61 What is the electronic structure of the Cu^{+2} ion?

A-61 Cu^{+2} is $3d^9$.

3d 4s 4p

↑↓ ↑↓ ↑↓ ↑↓ ↑ __ __ __ __

Q-62 If the $[Cu(NH_3)_4]^{+2}$ complex is dsp^2 hybridized, what configuration would you predict for the ion?

A-62 Square planar

Q-63 If the $[Cu(NH_3)_4]^{+2}$ complex has one unpaired electron, what value of μ, the magnetic moment, would be predicted for the ion?

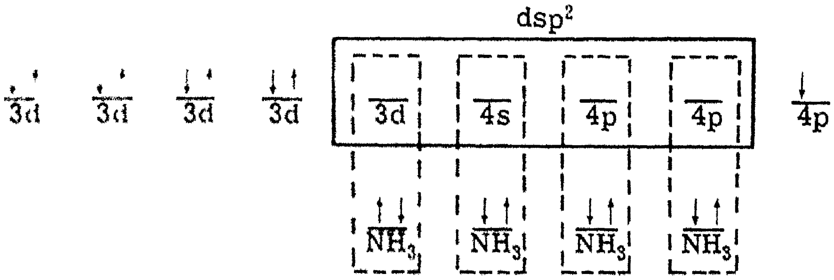
A-63 If $n = 1$

$\mu = \sqrt{n(n+2)}$

$= \sqrt{3} = 1.7$ B.M.

Q-64 Predict an electronic structure for the $[Cu(NH_3)_4]^{+2}$ complex.

A-64 $[Cu(NH_3)_4]^{+2}$



Note that an electron has been promoted from the 3d to the 4p orbital.

Q-65 What is the electronic structure of the Ni^{+2} ion?

A-65 Ni^{+2} is $3d^8$.

Q-66 If the $[Ni(NH_3)_6]^{+2}$ ion is sp^3d^2 hybridized, what configuration would be predicted for the complex?

A-66 Octahedral

Q-67 If the $[Ni(NH_3)_6]^{+2}$ ion has two unpaired electrons, what value of μ, the magnetic moment, would be predicted for the complex?

A-67 $n = 2$

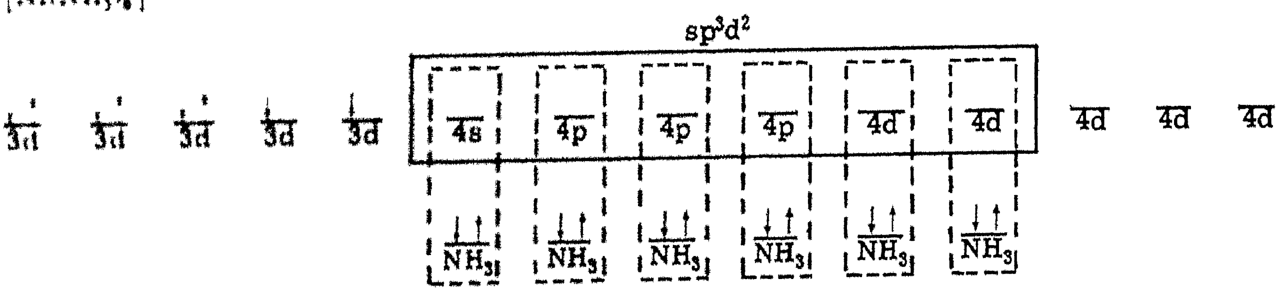
$\mu = \sqrt{n(n+2)}$

$= \sqrt{2(2+2)} = \sqrt{8}$

$= 2.8$ B.M.

Q-68 Predict an electronic structure for the $[Ni(NH_3)_6]^{+2}$ complex.

A-68 $[Ni(NH_3)_6]^{+2}$



S-4 One method of analyzing for ions in solution depends on complex ion formation. For example, Ag^+ ion forms a complex ion with excess NH_4OH while Pb^{+2} ion does not. Thus, a solution known to contain either Ag^+ or Pb^{+2} ion could be analyzed by the addition of excess NH_4OH. If the solution contained Pb^{+2} ion, white $Pb(OH)_2$ would be precipitated and would not dissolve in excess NH_4OH. If the solution contained Ag^+ ion, brown Ag_2O would be precipitated initially and would dissolve in excess NH_4OH.

$$Ag^+ + 2NH_3 \rightleftarrows Ag(NH_3)_2{}^+$$

Below is a periodic chart showing the ions which readily form complex ions with NH_3 by simply adding NH_4OH in excess. Study the table, and then proceed to the next questions which are designed to help you memorize this table

I_A	II_A	III_B	IV_B	V_B	VI_B	VII_B	VIII			I_B	II_B	III_A	IV_A	V_A	VI_A	VII_A
H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	$\boxed{Co}$	$\boxed{Ni}$	$\boxed{Cu}$	$\boxed{Zn}$	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	$\boxed{Rh}$	$\boxed{Pd}$	$\boxed{Ag}$	$\boxed{Cd}$	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	$\boxed{Ir}$	$\boxed{Pt}$	$\boxed{Au}$	$\boxed{Hg}$	Tl	Pb	Bi	Po	At

$\boxed{}$ ions which form complex ions

Q-69 If a solution of Al^{+3} ions and Cu^{+2} ions is treated with a small amount of NH_4OH, a precipitate is formed. What are the formulas of the salts precipitated?

A-69 $Al(OH)_3$
$Cu(OH)_2$

Q-70 If the precipitate is treated with excess NH_4OH, the $Cu(OH)_2$ dissolves, but the $Al(OH)_3$ does not. Write the equation for the reaction. The complex formed contains four NH_3 molecules.

A-70 $Cu(OH)_2 + 4NH_3 \rightleftarrows Cu(NH_3)_4{}^{+2} + 2OH^-$

Q-71 If a solution of Bi^{+3} and Ni^{+2} ions is treated with a small amount of NH_4OH, a precipitate is formed. What are the formulas of the salts precipitated?

A-71 $Bi(OH)_3$
$Ni(OH)_2$

Q-72 If the precipitate is treated with excess NH_4OH, the $Ni(OH)_2$ dissolves, but the $Bi(OH)_3$ does not. Write the equation for the reaction. The complex ion formed contains six NH_3 molecules.

A-72 $Ni(OH)_2 + 6NH_3 \rightleftharpoons Ni(NH_3)_6^{+2} + 2OH^-$	Q-73 The reaction of Mn^{+2} with NH_4OH is $Mn^{+2} + 2NH_3 + 2H_2O \rightarrow Mn(OH)_2 + 2NH_4^+$ Could a solution which was known to contain either Mn^{+2} or Cu^{+2} ions be analyzed using only NH_4OH?
A-73 Yes. Addition of NH_4OH would form a precipitate. If the precipitate did not dissolve in excess NH_4OH, Mn^{+2} would be present. If the precipitate dissolved in excess NH_4OH, Cu^{+2} would be present	Q-74 The reaction of Mg^{+2} with NH_4OH is $Mg^{+2} + 2NH_3 + 2H_2O \rightarrow Mg(OH)_2 + 2NH_4^+$ How could a solution known to contain either Mg^{+2} or Ni^{+2} ions be analyzed?
A-74 Treat the solution with NH_4OH. If the precipitate were $Ni(OH)_2$, it would dissolve in excess NH_4OH. $Mg(OH)_2$ would not dissolve	Q-75 The reaction of Fe^{+3} ions with NH_4OH is $Fe^{+3} + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3 + 3NH_4^+$ How could a solution known to contain either Fe^{+3} or Co^{+2} be analyzed? Write equations for the reactions. (The cobalt complex contains six NH_3 molecules.)
A-75 React the solution with NH_4OH. Possible reactions: $Fe^{+3} + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3 + 3NH_4^+$ $Co^{+2} + 2NH_3 + 2H_2O \rightarrow Co(OH)_2 + 2NH_4^+$ Treat the precipitate with excess NH_4OH. If the precipitate were $Co(OH)_2$ it would dissolve. $Fe(OH)_3$ would not dissolve. $Co(OH)_2 + 6NH_3 \rightleftharpoons Co(NH_3)_6^{+2} + 2OH^-$	Q-76 The reaction of Cr^{+3} with NH_4OH is $Cr^{+3} + 3NH_3 + 3H_2O \rightarrow Cr(OH)_3 + 3NH_4^+$ How could a solution known to contain either Zn^{+2} or Cr^{+3} be analyzed? Write equations for the reactions. (The zinc complex contains four NH_3 molecules.)
A-76 Add NH_4OH to the unknown solution. Possible reactions: $Cr^{+3} + 3NH_3 + 3H_2O \rightarrow Cr(OH)_3 + 3NH_4^+$ $Zn^{+2} + 2NH_3 + 2H_2O \rightarrow Zn(OH)_2 + 2NH_4^+$ Treat the precipitate with excess NH_4OH. If the precipitate were $Zn(OH)_2$, it would dissolve. $Cr(OH)_3$ would not dissolve. $Zn(OH)_2 + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{+2} + 2OH^-$	Q-77 Addition of NH_4OH to an As(III) solution gives no precipitate. How could As(III) be identified in a solution known to contain either As(III), Mn^{+2}, or Cu^{+2}?
A-77 If addition of NH_4OH does not yield a precipitate, As(III) is present. A precipitate indicates either Mn^{+2} or Cu^{+2}.	Q-78 Could you determine whether a precipitate was $Mn(OH)_2$ or $Cu(OH)_2$? Write equations for the reactions.
A-78 Addition of excess NH_4OH to the precipitate will dissolve $Cu(OH)_2$ but not the $Mn(OH)_2$. $Cu(OH)_2 + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{+2} + 2OH^-$	Q-79 Addition of NH_4OH to a solution of K^+ ions gives no precipitate. How could a solution known to contain either K^+, Ni^{+2} or Bi^{+3} be analyzed?

A-79 Add NH_4OH to the solution If no precipitate forms, the solution contains K^+. A precipitate indicates either Ni^{+2} or Bi^{+3}. If the precipitate dissolves in excess NH_4OH, it is $Ni(OH)_2$

$Ni^{+2} + 2NH_3 + 2H_2O \rightarrow Ni(OH)_2 + 2NH_4^+$

$Bi^{+3} + 3NH_3 + 3H_2O \rightarrow Bi(OH)_3 + 3NH_4^+$

$Ni(OH)_2 + 6NH_3 \rightleftarrows Ni(NH_3)_6^{+2} + 2OH$

Q-80 The reaction of Sn^{+4} with NH_4OH is

$Sn^{+4} + 4NH_3 + 4H_2O \rightarrow Sn(OH)_4 + 4NH_4^+$

How could a solution known to contain either Sn^{+4} or Ag^+ be analyzed?

A-80 Addition of NH_4OH would precipitate both Sn^{+4} and Ag^+

$Sn^{+4} + 4NH_3 + 4H_2O \rightarrow Sn(OH)_4 + 4NH_4^+$

$2Ag^+ + 2NH_3 + H_2O \rightarrow Ag_2O + 2NH_4^+$

Excess NH_4OH would dissolve Ag_2O but not $Sn(OH)_4$

$Ag_2O + 4NH_3 + H_2O \rightarrow 2Ag(NH_3)_2^+ + 2OH^-$

Q-81 Which of the following ions would yield a precipitate with NH_4OH? (The NH_4OH is not in excess.) Write the formula of the precipitates formed.

Cu^{+2}

Mg^{+2}

Co^{+2}

K^+

A-81 $Cu(OH)_2$

$Mg(OH)_2$

$Co(OH)_2$

Q-82 Which of the precipitates in A-81 would dissolve in excess NH_4OH (i.e., form a complex ion)? Write the formula of the ion formed.

A-82 $Cu(NH_3)_4^{+2}$

$Co(NH_3)_6^{+2}$

Q-83 Treatment of a Ba^{+2} ion solution with NH_4OH produces no precipitate. How could a solution known to contain either Ba^{+2}, Mg^{+2} or Co^{+2} be analyzed? Write the equations

A-83 React the solution with NH_4OH. If no precipitate formed, Ba^{+2} would be present If a precipitate formed it could be $Mg(OH)_2$ or $Co(OH)_2$

$Mg^{+2} + 2NH_3 + 2H_2O \rightarrow Mg(OH)_2 + 2NH_4^+$

$Co^{+2} + 2NH_3 + 2H_2O \rightarrow Co(OH)_2 + 2NH_4^+$

Addition of excess NH_4OH would dissolve $Co(OH)_2$ but not $Mg(OH)_2$.

$Co(OH)_2 + 6NH_3 \rightleftarrows Co(NH_3)_6^{+2} + 2OH^-$

Q-84 Which of the following will yield a precipitate with NH_4OH? (The NH_4OH is not in excess.)

As(III)

Zn^{+2}

Al^{+3}

Write the formula of precipitates formed.

A-84 $Zn(OH)_2$

$Al(OH)_3$

Q-85 Which of the hydroxides in A-84 will dissolve in excess NH_4OH? Write the formula of the ion(s).

A-85 $Zn(NH_3)_4^{+2}$

Q-86 Treatment of a solution of Sb^{+3} with NH_4OH gives a precipitate of $Sb(OH)_3$.

$Sb^{+3} + 3NH_3 + 3H_2O \rightarrow Sb(OH)_3 + 3NH_4^+$

How could a solution known to contain either Sb^{+3} or Zn^{+2} be analyzed?

A-86 Addition of NH_4OH would precipitate either $Zn(OH)_2$ or $Sb(OH)_3$. Excess reagent would dissolve only $Zn(OH)_2$

$$Zn(OH)_2 + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{+2} + 2OH^-$$

Q-87 Addition of NH_4OH to a solution of Pb^{+2} ions produces a precipitate of $Pb(OH)_2$.

$$Pb^{+2} + 2NH_3 + 2H_2O \rightarrow Pb(OH)_2 + 2NH_4^+$$

How could a solution known to contain Cu^{+2} or Pb^{+2} be analyzed?

A-87 Addition of NH_4OH would precipitate either $Pb(OH)_2$ or $Cu(OH)_2$. If the precipitate dissolved in excess NH_4OH, it would be $Cu(OH)_2$

Q-88 Which of the following will dissolve in excess NH_4OH?

$Fe(OH)_3$

$Ni(OH)_2$

$Co(OH)_2$

$Bi(OH)_3$

A-88 $Ni(OH)_2$

$Co(OH)_2$

Q-89 Which of the following will dissolve in excess NH_4OH?

$Cu(OH)_2$

$Mn(OH)_2$

$Cr(OH)_3$

$Zn(OH)_2$

A-89 $Cu(OH)_2$

$Zn(OH)_2$

Q-90 Which of the following will yield a precipitate with NH_4OH? (The NH_4OH is not in excess.)

K^+

Al^{+3}

Mg^{+2}

Pb^{+2}

Write the formulas of the precipitates

A-90 $Al(OH)_3$

$Mg(OH)_2$

$Pb(OH)_2$

Q-91 Will any of the hydroxides in A-90 dissolve in excess NH_4OH? (i. e., form an ammonia complex)

A-91 No.

Q-92 Addition of NH_4OH to a solution of Na^+ ions produces no precipitate. How could a solution known to contain one of the following ions be analyzed?

Na^+ Fe^{+3} Ni^{+2}

Write equations for the reactions.

A-92 If no precipitate forms when NH_4OH is added, Na^+ is present A precipitate indicates either Fe^{+3} or Ni^{+2}. If the precipitate dissolves in excess NH_4OH, Ni^{+2} is present

$$Fe^{+3} + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3 + 3NH_4^+$$

$$Ni^{+2} + 2NH_3 + 2H_2O \rightarrow Ni(OH)_2 + 2NH_4^+$$

$$Ni(OH)_2 + 6NH_3 \rightleftarrows Ni(NH_3)_6^{+2} + 2OH^-$$

Q-93 How could a solution known to contain one of the following ions be analyzed?

K^+ Bi^{+3} Co^{+2}

Write equations for the reactions

A-93 If no precipitate forms when NH_4OH is added, K^+ is present A precipitate indicates either Bi^{+3} or Co^{+2} If the precipitate dissolves in excess reagent, Co^{+2} is present

$$Bi^{+3} + 3NH_3 + 3H_2O \rightarrow Bi(OH)_3 + 3NH_4^+$$

$$Co^{+2} + 2NH_3 + 2H_2O \rightarrow Co(OH)_2 + 2NH_4^+$$

$$Co(OH)_2 + 6NH_3 \rightleftarrows Co(NH_3)_6^{+2} + 2OH^-$$

Q-94 Which of the following hydroxides will dissolve in excess NH_4OH?

$Bi(OH)_3$

$Sb(OH)_3$

$Fe(OH)_3$

Write the formulas of the complex ions formed

A-94 None of the hydroxides form complex ions with NH_3

Q-95 Which of the following form complex ions with excess NH_4OH?

$Al(OH)_3$

$Cr(OH)_3$

Ag_2O

Write formulas for the complex ions formed.

A-95 $Ag(NH_3)_2^+$

R-5 Ions may be separated and identified by reactions which form complex ions.

S-5 Many ions may be separated and identified by using either NaOH or NH_4OH The analysis of many more combinations of ions is possible by making use of both amphoteric and complex ion forming properties

Q-96 An acidic solution was known to contain only one ion, Ag^+, Cd^{+2}, or Sn^{+4}. The solution was made basic with NH_4OH. A precipitate which formed initially dissolved in excess NH_4OH. What conclusions could be drawn?

A-96 $Sn(OH)_4$ would precipitate under the conditions used, but would not dissolve in excess NH_4OH. Therefore, Sn^{+4} must be absent. Both Ag^+ and Cd^{+2} would form a precipitate which would dissolve in excess NH_4OH to form a complex ion.

Q-97 When the acidic solution described in the preceding question was made basic with NaOH, a black precipitate formed. What conclusion could be drawn?

(Hint: $Cd(OH)_2$ is white.)

A-97 The precipitate was Ag_2O. Ag^+ was present in the solution.

Q-98 An acidic solution could contain any one of the ions Al^{+3}, Co^{+2}, or Zn^{+2}. The acidic solution was made basic with NH_4OH. A precipitate which formed initially dissolved in excess NH_4OH. Another portion of acidic solution was made basic with NaOH, a precipitate which formed initially dissolved in excess NaOH. What conclusions can be drawn?

A-98 Co^{+2} and Zn^{+2} both form complex ions, but only Zn^{+2} forms a complex ion and is also amphoteric. Zn^{+2} was present.

Q-99 How could the following ions be separated?

Ni^{+2}, Mn^{+2}, Al^{+3}

A-99 Addition of NaOH to the solution would precipitate all three ions. Addition of excess NaOH to the precipitate would dissolve $Al(OH)_3$. Addition of excess NH_4OH to the precipitate would dissolve $Ni(OH)_2$.

Q-100 How could a mixture containing one of the following ions be analyzed?

As(III), Cr^{+3}, Ag^+

A-100 Addition of NH_4OH would precipitate $Cr(OH)_3$ and Ag_2O. As(III) would not form a precipitate. Ag_2O would dissolve in excess NH_4OH. $Cr(OH)_3$ would not dissolve in NH_4OH.

Q-101 When excess NaOH is added to Cr^{+3} ion, the ion formed (CrO_2^-) is emerald green. How could a solution which may contain any of the following ions be analyzed?

Cr^{+3}, Co^{+2}, Bi^{+3}

A-101 Addition of NaOH to the solution will precipitate all three ions. Addition of excess NaOH to the precipitate will form the green CrO_2^- ion. Addition of excess NH_4OH to the precipitate will form the $Co(NH_3)_6^{+2}$ ion and leave $Bi(OH)_3$ as a precipitate.

Q-102 Addition of excess NH_4OH to Cu^{+2} ion forms the complex ion $Cu(NH_3)_4^{+2}$ which is blue. How could a solution which may contain any of the following ions be analyzed?

Cu^{+2}, Sb^{+3}, Mg^{+2}

A-102 Addition of NH_4OH to the solution will precipitate all three ions. Addition of excess NH_4OH to the precipitate will form the blue $Cu(NH_3)_4^{+2}$ ion. Addition of excess NaOH to the precipitate will form the SbO_3^{-3} ion and leave $Mg(OH)_2$ as a precipitate.

Q-103 A solution may contain any of the following ions.

Al^{+3}, Co^{+2}, As(III), Zn^{+2}

Upon addition of a combination of NH_4OH and NaOH a precipitate formed initially, but dissolved when an excess of the combination was added. What ions are present, are absent, can't be determined?

A-103 Zn^{+2} is the only ion which is known to be present. Al^{+3} and Co^{+2} are absent. As(III) can't be determined.

Q-104 How could a solution known to contain one of the following ions be analyzed?

Pb^{+2}, Cd^{+2}, Ca^{-2}

A-104 Addition of NaOH would precipitate any of the three ions. Addition of excess NaOH to the precipitate would dissolve $Pb(OH)_2$. Addition of excess NH_4OH to the precipitate would dissolve $Cd(OH)_2$. $Ca(OH)_2$ would not dissolve in either excess NH_4OH or NaOH.

By using both NaOH and NH_4OH, a large variety of separations and identifications of ions may be made.

NOTES